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RESEARCH PAPER RP858

Part of Journal of Research of the National Bureau of Standards, Volume 16, February 1936

A STANDARD SOURCE OF ULTRAVIOLET RADIATION FOR CALIBRATING PHOTOELECTRIC DOSAGE INTENSITY METERS

By W. W. Coblentz and R. Stair

ABSTRACT

The advantages and disadvantages of sources emitting either a continuous or a discontinuous spectrum are considered in connection with the use of such lamps as a standard of ultraviolet radiation.

It is shown that because of the high intensity and favorable distribution of the ultraviolet emission lines at 2967 to 3132 A, the quartz mercury-arc lamp is well adapted for standardizing photoelectric ultraviolet dosage intensity meters in absolute units.

A description is given of the installation of a commercial 110-volt vertical quartz mercury Uviarc lamp, and of methods of calibrating its ultraviolet output in absolute units.

By calibrating photoelectric ultraviolet intensity meters against a laboratory standard, a great reduction is effected in equipment required for field measurements of ultraviolet solar radiation.

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I. INTRODUCTION

The evaluation, in absolute units, of the energy in a given spectral band of radiation, by a filter method of radiometry involves two measurements: (1) the spectral quality (the spectral-energy distribution), and (2) the total intensity (the radiant flux) within and adjacent to the band of wave lengths under investigation.

Based upon the report [1] [1] of the favorable performance of a balanced ("differential") thermopile and filter radiometer [2, 3], at the Copenhagen Meeting in 1932, the International Committee on Measurement and Standardization of Ultraviolet Radiation for Use in Medicine recommended to the International Congress on Light the evaluation of ultraviolet-radiation stimuli on a physical (radiometric) basis, in absolute units, by means of a nonselective radiometer (thermopile) and filters [4].

[1] Numbers in brackets refer to references and notes at the end of this paper.

The thermopile and filter apparatus is essentially a primary standard of evaluation of ultraviolet radiation [2, 3, 13]. For field work the writers have recently devised a portable ultraviolet meter, which consists of a photoelectric cell, balanced amplifier, and microammeter [5]. This type of ultraviolet meter requires standardization either against the thermoelectric meter [2], which initially was calibrated against a standard of radiation or against an absolute thermopile [7], in order to standardize the microammeter reading in absolute value.

Heretofore the writers have calibrated the photoelectric ultraviolet meter directly against the type of source (the sun) under investigation, by making simultaneous measurements with the thermoelectric meter [2, 3] which initially was calibrated in absolute value against a standard of radiation [6, 8]; the photoelectric cell and filters being used to determine the spectral quality of the source (the sun) at the time of making the energy measurements with the balanced thermopile.

Without the use of complicated auxiliary apparatus the thermopile (with filters) is not sufficiently sensitive, and, hence, not well adapted for determining the spectral quality of the short wave length ultraviolet radiation of the sun; but it is the best instrument to evaluate the energy in absolute value.

Hence, to simplify the equipment for field work such as was conducted by one of the writers (W. W. C.) in Arizona, and more recently at San Juan, P. R. (where preliminary tests [9] of this method have already been made), and to simplify the computations, a photoelectric ultraviolet-intensity meter [5] is used to determine both the spectral quality and the total intensity in a given band of wave lengths of ultraviolet in sunlight.

The problem, therefore, was to devise a laboratory method of calibrating the photoelectric meter (the microammeter-scale reading) in absolute units, so that the response will be a measurement, in absolute value, of the ultraviolet intensity in sunlight [14].

In a forthcoming paper two closely agreeing methods of evaluation of ultraviolet solar radiation will be described: (1) by means of a balanced thermopile (with filters), which is calibrated in absolute value against a standard of thermal radiation [6, 8], and (2) by means of a photoelectric cell of titanium, calibrated in absolute value against a standard of ultraviolet radiation.

This amounts to a calibration of the photoelectric cell against a lamp in the laboratory, instead of calibrating it against the sun as a source (by making closely simultaneous measurements with the balanced thermopile, and the photoelectric meter) which, as already mentioned, was the previous procedure.

The manner of calculating the data, which is somewhat complex, will be described in the above-mentioned forthcoming paper on the evaluation of ultraviolet radiation in sunlight, for which purpose the whole scheme was devised.

The object of the present communication is to describe a convenient standard source of ultraviolet radiation, which consists of a vertical mercury-in-quartz arc lamp that is readily obtainable in commerce at a price that is not prohibitive, and which, with careful use, promises to have a long life.

1. THE QUARTZ MERCURY-ARC LAMP VERSUS THE TUNGSTEN-FILAMENT LAMP AS A STANDARD SOURCE OF ULTRAVIOLET RADIATION

The following are some of the advantages in using the quartz mercury arc as a standard source of ultraviolet radiation; which source is particularly applicable for calibrating photoelectric cells used in evaluating the ultraviolet radiation, of wave lengths 3132 A and shorter, used for therapeutic purposes:

(1) The ultraviolet radiation of the so-called hot quartz mercury lamp is emitted in a few, conveniently distributed, intense emission lines, superposed upon a weak background of continuous spectral emission that causes little or no difficulty in correcting for spectral purity.

(2) The relative spectral intensities of these emission lines, as a function of the temperature, the energy input, and the aging of the lamp, are readily determined.

(3) The quartz mercury arc is in common use for determining (a) the transmission of the spectrometer used in measuring the spectral intensities of the emission lines in absolute values, (b) the spectral transmission of the filters used in the filter method of radiometery, (c) the spectral response of the photoelectric cell, used in measuring ultraviolet radiation, and (d) the effects of ultraviolet in biological investigations.

(4) The emission line at 2967 A, emitted by the quartz mercury-arc lamp, evaluated in absolute units, was found useful in standardizing skin sensibility, in connection with investigations of the erythemal reaction produced by different sources of ultraviolet radiation [3], and recently this emission line was used in connection with the study of the effect of environment upon the production of erythema [10].

(5) The total ultraviolet in a given spectral band can be determined in absolute units, by measuring the intensities in the individual lines in absolute value, as was done successfully by seven research laboratories [11], using different kinds of spectroradiometers, and quartz mercury-arc lamps that were interchanged between the various laboratories. If the participating laboratories had used the most modern apparatus and methods there would have resulted a still closer agreement in the measurements.

(6) The total radiation, in absolute value, included in the spectral band of wave lengths 3132 A and shorter (of special interest in therapy) can be accurately evaluated, as indicated by the agreement in the values obtained by summation of the intensities of the individual spectral lines, and by integrated measurements of the undispersed radiation, using a balanced thermopile and filter radiometer [2, 3, 11].

(7) The use of a discontinuous spectrum of intense emission lines, readily permits testing the accuracy of the energy evaluation, as for example, in the studies of the germicidal action of ultraviolet radiation, conducted by Coblentz and Fulton [12], in which practically exact agreement was found between the observed and the calculated transmissions of the filters used to determine the spectral range of the germicidal action.

(8) In calibrating a modern photoelectric cell which is insensitive to wave lengths longer than about 3300 A, and in which the short-

wave-length response is limited (at about 2800 A) by its inclosure of Corex D glass, practically only the strong emission lines at 2967, 3024, and 3132 A are effective.

The energy value of these few lines is easily determined in absolute units, by two methods [2, 3, 11], and from a knowledge of the spectral-response curve of the photoelectric cell there is obtained the true scale reading of the microammeter [5] that would have resulted if the photoelectric cell had been nonselective in spectral response.

From the viewpoint of cost, a gas-filled tungsten lamp has been considered for use as a standard source of ultraviolet radiation for calibrating photoelectric ultraviolet meters. The following are some of the disadvantages in using, as a standard source of ultraviolet radiation, a lamp which emits a continuous spectrum, for example, a gas-filled tungsten lamp:

(1) The spectral intensity of the ultraviolet, particularly of wave lengths shorter than 3000 A, emitted by a tungsten-filament lamp is low, and, hence difficult to determine accurately in absolute value.

(2) There is difficulty and uncertainty in correcting for spectral purity in reducing the observed intensities in the continuous spectrum, from the prismatic to the normal spectral distribution—a necessary procedure, since different laboratories use spectroradiometers having different dispersion and transmission constants.

(3) Owing to uncertainty in spectral purity, there is difficulty in establishing the long-wave-length limit, say at 3130 A, of the cut-off, in integrating a spectral band of radiation such as, for example, the band of ultraviolet radiation, including for all practical purposes the wave length 3132 A (and shorter wave lengths), which is recognized as having a therapeutic value in healing rickets.

(4) Based upon the experience of one of the writers (W. W. C.), extending over a period of three decades, the accurate mapping of the continuous spectrum of low intensity is extremely difficult and uncertain, particularly the evaluation of the energy in a narrow spectral band, in absolute units, because of the uncertainty of the corrections for absorption in the spectrometer.

(5) The continuous spectrum is not readily adapted for making the calculations required in connection with the evaluation of the spectral response of the photoelectric cells or for checking the accuracy of the calibrations, by comparing the observed with the calculated filter transmissions.

2. TESTS OF THE EMISSION LINE 2967 A AS A STANDARD SOURCE OF RADIATION

For calibrating a photoelectric ultraviolet-intensity meter [5] in absolute value, the simplest procedure would appear to be to observe the microammeter-scale reading on exposure of the photoelectric cell to a strong emission line, the energy value of which is easily determined in absolute units [3]. Then the true scale reading would be obtained by dividing the observed scale reading by the efficiency of the photoelectric response for that wave length. The resulting microammeter reading would then be relatively the same as that of a spectrally nonselective radiometer.

The writers have attempted to calibrate their photoelectric ultraviolet-intensity meter [5], in absolute value, by means of homo-

geneous radiation of wave length 2967 A, because this emission line has a number of advantages which make it useful as a standard in erythemal and photobiological investigations [1, 3, 13].

However, the attempt to calibrate the photoelectric ultraviolet meter [5] used in evaluating the ultraviolet in sunlight, by employing the emission line of mercury, at 2967 A as a standard, was not very successful, owing to the manner of construction of the photoelectric cell (the heavy-wire anode occupies the center of the field), which caused difficulties in operating the device at the exit slit of the spectroradiometer used in isolating the emission line 2967 A.

Hence, since the radiation from the quartz mercury arc, effective on the photoelectric cells used by the writers, can be confined practically to four emission lines (at 2894, 2967, 3024, and 3132 A, by using a filter of Corex D glass), which can be accurately evaluated in absolute units [2, 3, 11], the writers have adopted this type of lamp as a standard source of ultraviolet radiation for calibrating photoelectric dosage intensity meters.

To attain the highest accuracy in the calibrations, the ultraviolet output of the lamp is determined with the balanced thermocouple and filters [2, 3], at the time the photoelectric measurements are made, and at the same distance from the lamp. This eliminates the difficulty of setting the photoelectric ultraviolet meter at a known distance from the lamp, and of operating the lamp at a fixed room temperature, which has a slight effect on the output at a given voltage.

Another procedure is to operate the lamp at a constant-energy input, in the burner, in an inclosure that is maintained closely at the same air temperature. In this manner a single standardization of the lamp against the balanced thermopile, at a fixed distance from the lamp, will suffice until the lamp shows signs of aging (blackening).

The reduction in intensity (aging by blackening of the part of the quartz tube surrounding the tungsten anode), and a possible unsteadiness of the radiation resulting from the constant flickering of the luminous column directly above the mercury cathode are eliminated by placing in front of the lamp a diaphragm, having an opening 30 mm in length, which limits the emission to the central portion of the lamp, about 30 mm in length.

In conclusion it is relevant to summarize the foregoing discussion by recalling that in previous solar ultraviolet measurements in the field (e. g., in Arizona) two sets of instruments were used to evaluate the ultraviolet in sunlight, (1) photoelectric cells and filters to measure the spectral quality, and (2) a balanced thermopile and filter radiometer to evaluate the total intensity of the ultraviolet, in absolute units.

By calibrating the portable ultraviolet intensity meter [5] against the herein-described standard source of ultraviolet radiation, it will not be necessary to carry the balanced thermopile outfit into the field. This was amply demonstrated in a recent calibration of a recording ultraviolet meter, and in an investigation of the spectral quality (ozone content) of the ultraviolet, in San Juan, P. R. [9], in which only the portable ultraviolet intensity meter was employed. Checked against the standard source, on the return, the calibration of the photoelectric cell was found unchanged; and since, as will be shown in a forthcoming paper, the evaluation of the ultraviolet in sunlight by the thermoelectric and the photoelectric methods is the same, there

is a considerable saving in time and expense in transportation, by using only the standard portable photoelectric meter [5], with several standardized photoelectric cells in reserve.

In view of the fact that in earlier communications the writers were opposed to the use of photoelectric cells as ultraviolet meters, it is relevant to add that recent improvements have overcome the objectionable features of earlier makes of photoelectric cells, in which there was great fatigue and in which the response depended upon the applied voltage and was not proportional to the intensity. As pointed out elsewhere [14] the modern, highly evacuated photoelectric cell of titanium or cadmium, with its selective spectral response confined to wave lengths shorter than 3300 A, in contrast with the nonselective response of the thermopile, appears to be an advantage instead of a disadvantage, at least in evaluating short wave length (2900 to 3300 A) ultraviolet solar radiation. This is owing to the fact the spectral-energy curve of the sun, in the region of 3300 to 4000 A, is not known with sufficient accuracy to calculate the energy in this spectral band, and there are no suitable filters to place over the thermopile, to completely eliminate this part of the spectrum and confine the measurements to the spectral band of wave lengths shorter than 3300 A, which is possible with a photoelectric cell that does not respond to wave lengths longer than about 3300 A. In recent measurements of solar ultraviolet radiation, the writers placed an especially selected filter of Corning Purple Corex glass, G 986–A, over the thermopile [2], thus reducing its spectral response principally to wave lengths shorter than about 4000 A, and apparently increasing the accuracy of the calculations of the results. In view of the complexity of the apparatus and experimental procedure involved in making the observations, the closely agreeing results obtained by the two methods of measurement (thermoelectric and photoelectric), appear to show that the data are substantially correct.

II. DESCRIPTION OF THE QUARTZ MERCURY-ARC LAMP

During the past several years the writers have used several types of d–c and a–c mercury-in-quartz arc lamps, operated in the horizontal and the vertical positions, for calibrating ultraviolet meters [14]. The earliest calibrations of ultraviolet meters were made with a Hanovia Luxor Model, a–c therapeutic lamp, which had a satisfactory performance but which, on account of its horizontal position, was not convenient to operate in front of a spectroradiometer.

The type of lamp adopted is the Cooper-Hewitt (General Electric Vapor Lamp Co.), 110-volt, vertical Uviarc, mercury-in-quartz arc lamp, which is the most convenient arrangement for all types of measurements, particularly with a spectroscope.

The clear part of the quartz tube, which is about 8 cm long between the electrodes and about 18 mm in diameter, is covered with a sheet of aluminum (W in fig. 1) having an opening 30 by 30 mm, which produces a symmetrical source free from the flickering noticeable over the lower mercury electrode and excludes the upper end, part of which may become blackened from the tungsten anode.

As shown diagrammatically in figure 1, the support for the quartz tube (the "burner") consists of a right-angle piece of aluminum A, attached to the nickel-plated iron rod R, in a support that permits

rotation of the arc into the horizontal position, which is necessary to start the arc. Adjustable clamp S serves as a stop to place the lamp in the same vertical position after each starting of the lamp.

The lamp rests in a porcelain or Pyrex support P, which insulates it from the aluminum frame. The top support of the lamp is a strip

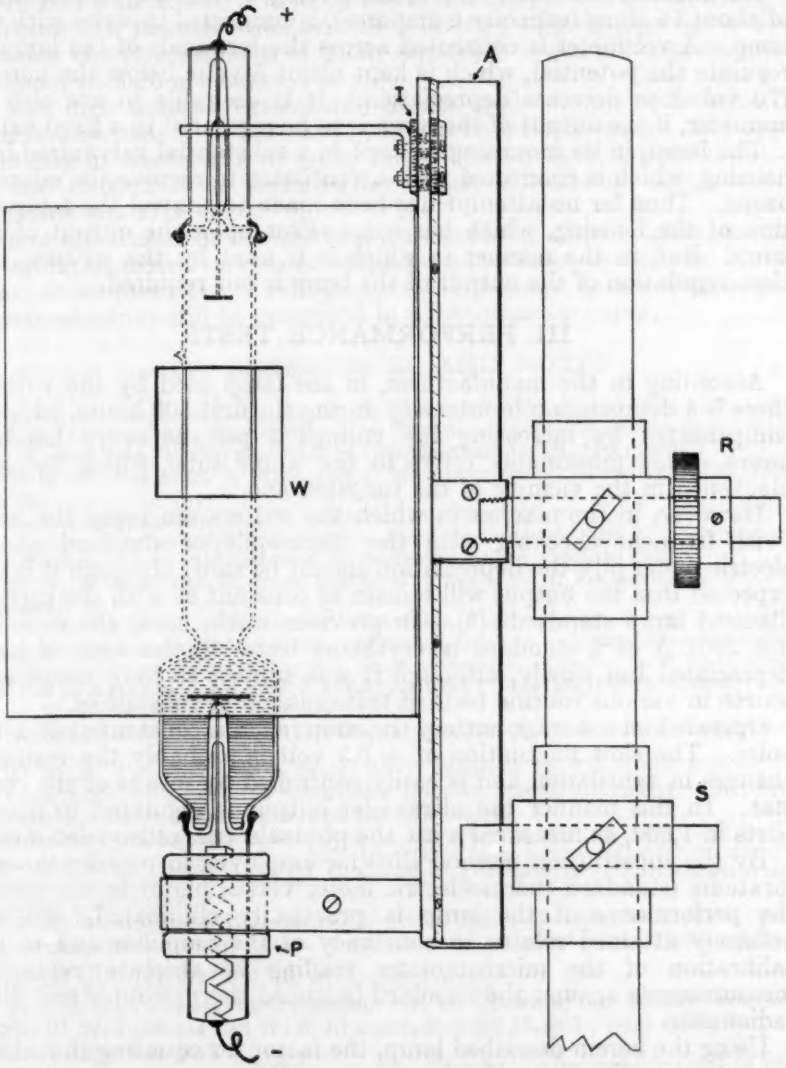

FIGURE 1.—*Mounting of ultraviolet radiation standard.*

of aluminum, which is insulated from the vertical support A by means of mica and asbestos, I.

The electrical connections (indicated diagrammatically) are thin pliable strips of brass, some 5 cm long at the free ends, which remain cool, and, hence, do not disintegrate by the heat of the electrodes. The lead-wires are soldered to these metal strips.

An aluminum shield W is securely attached to the vertical support A, and forms a benchmark for measuring distances. With the exception of the aluminum support A, the remaining part of the lamp holder consists of a tripod, rods, and right-angle clamps, which form the equipment of the average physics laboratory.

An ordinary laboratory rheostat, having a ribbon-type resistance of about 18 ohms (capacity 6 amperes), is connected in series with the lamp. A voltmeter is connected across the terminals of the lamp to regulate the potential, which is kept about 5 volts below the normal (70 volts) to decrease depreciation. It is desirable to use also an ammeter, if the output of the lamp is to be regulated to a fixed value.

The lamp, in its mounting, is kept in a substantial galvanized-iron housing, which is connected with a ventilator to remove the odors of ozone. Thus far no attempt has been made to control the temperature of the housing, which has some effect upon the output of the lamp. But, in the manner in which it is used by the writers, this close regulation of the output of the lamp is not required.

III. PERFORMANCE TESTS

According to the manufacturer, in the lamp used by the writers, there is a depreciation in intensity during the first 500 hours, which is compensated by increasing the voltage 3 percent every hundred hours. This presumably refers to the whole tube, which becomes blackened in the vicinity of the tungsten anode.

However, in the manner in which the writers are using the lamp (with frequent checking with the thermopile or standard photoelectric meter [5]), the depreciation should be slow; although it is not expected that the output will remain as constant as with the carbon-filament lamp standards [8]. In previous work, using the emission line 2967 A as a standard in erythema tests [4], this type of lamp depreciated but slowly, although it was subject to hard usage as a source in various routine tests of transmission of substances.

Operated on a storage battery the lamp remains constant at 65 ± 0.3 volts. The slow fluctuation of ± 0.3 volt is probably the result of changes in ventilation and is easily controlled by means of the rheostat. In this manner the ultraviolet output is regulated to 2 or 3 parts in 1,500, as measured with the photoelectric ultraviolet meter.

By the substitution method thus far employed in making the calibrations (standard thermoelectric meter versus photoelectric meter) the performance of the lamp is practically eliminated, and the accuracy attained relates to constancy of the amplifier and to the calibration of the microammeter reading in absolute value, by measurements against the standard balanced thermocouple and filter radiometer.

Using the herein-described lamp, the factor for equating the microammeter reading into absolute units (microwatts per cm^2) using photoelectric cell Ti–1, determined on different days, was 9.33 and 8.97, respectively, the whole apparatus having been dismounted (the window of the photoelectric cell was freed from dust) and reset in the meantime. The dust particles, which became attached by an electric charge on the glass, would reduce the transmission by 1 or more percent, and on removal would decrease the factor 9.33 to a lower value, as observed. Hence, the deviation of 2 percent from the

mean value (9.15) is ascribable partly to dust adhering to the window of the photoelectric cell. The average of four calibrations, made between January 22 and December 16, 1935, using two Uviarc lamps, is 9.06—a difference of only 1 percent from the most recent and presumably the most reliable determinations.

In this connection, it is to be noted that there is great difficulty in keeping the photoelectric cells and filters perfectly free from electrically charged particles of dust, especially when working in a dry climate, at high altitudes.

The high accuracy attainable in the calibration of photoelectric ultraviolet meters in the laboratory is entirely illusory. It has no meaning in attempting to evaluate the constantly changing intensity of the ultraviolet in sunlight, for which this double check in the calibration was devised.

The agreement in the absolute values of the ultraviolet intensities in sunlight, under various atmospheric conditions, as deduced by the two above-described methods of measurement (photoelectric and thermoelectric) will be described in a forthcoming paper.

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Description of the evaluation of ultraviolet in different sources by means of a balanced thermocouple and filter radiometer, used as a dosage intensity meter; p. 769 enumerates the advantages in using homogeneous radiation of wave length 2967 A as a standard source for radiometric and physiological (erythema) tests.

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Report on the Copenhagen meeting of the Second International Congress on Light.

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Description of a portable ultraviolet intensity meter consisting of a photoelectric cell, balanced amplifier, and microammeter.

Considering the progress described in the present paper in producing such a standard, the statement (on p. 232) that there is as yet no (simple) standard of ultraviolet radiation for accurately testing the constancy of photoelectric cells requires qualification.

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WASHINGTON, December 16, 1935.

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RESEARCH PAPER RP859

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TREATMENT OF OFFSET PAPERS FOR OPTIMUM REGISTER

By Charles G. Weber and Martin N. V. Geib

ABSTRACT

Paper distortion and misregister of color prints are often serious problems in offset printing; even when the paper is conditioned to equilibrium with the pressroom air and printed under controlled atmospheric conditions. Hence, a study was made of the relation of the hygrometric condition of papers at the start of the first print to changes in moisture content during printing, and to the register of prints.

Experimental printings were made on papers in various hygrometric conditions relative to the surrounding atmosphere, and the behavior during multicolor printing was determined by finding the moisture-content changes, dimensional distortion, and closeness of register. Papers conditioned to equilibrium with the pressroom air by the usual method expanded during the first few printings so that succeeding colors printed inside the first. It was found possible to maintain constant dimensions by two methods of conditioning. Papers conditioned first at a very high relative humidity, then to equilibrium with the pressroom atmosphere by desorption, remained fairly constant. Also, papers prepared for printing by conditioning to equilibrium with relative humidity 5 to 8 percent above the pressroom condition gave very satisfactory results. The latter procedure is the more feasible for commercial practice as it requires conditioning the paper but once. All dimensional changes during printing were accounted for by changes in moisture content, and no evidences of mechanical stretch were found.

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I. INTRODUCTION

The effects of paper conditioning on the hygrometric changes of paper, and the constancy of its dimensions are of great importance in offset printing, because the most serious difficulty encountered, that of obtaining close register of successive color prints, is involved. Lack of information on the subject has resulted in failure to obtain the full benefits of costly air-conditioning equipment and often in wrongfully attributing misregister to the character of the paper being printed rather than to its hygrometric condition.

In previous articles on the influence of atmospheric changes on moisture content and dimensions [1] of paper and the relation of paper

[1] Weber and Snyder, BS J. Research 12, 53 (1934) RP633.

properties to register,[2] the importance of direction coefficient of expansion in paper and of constant atmospheric conditions during printing were pointed out. Further register studies revealed that paper commonly changes dimensions during printing, even when adjusted to moisture equilibrium with the pressroom air and printed under constant conditions of humidity and temperature. Hence the effects of various conditioning factors on changes of moisture content and distortion during printing were investigated in the air-conditioned offset printing plant of the Coast and Geodetic Survey of the U. S. Department of Commerce.

This is one of a series of studies made to assist lithographers in reducing serious economic losses caused by difficulties in offset printing. The work is being done with the active cooperation of the Lithographic Technical Foundation and financial assistance of several offset-paper manufacturers. The industry assists through an advisory committee composed of lithographers, paper manufacturers, and printing-equipment manufacturers under the chairmanship of R. F. Reed, Director of Lithographic Research, University of Cincinnati.

II. PROPERTIES OF OFFSET PAPERS STUDIED

Three different papers were used in the investigation: a chemical wood-fiber offset paper, found in previous studies to have low machine-direction expansion;[3] a rag-content bond; and a 100-percent rag chart paper, surface sized with glue. Although no attempt was made to study the response of different papers, the three papers used represent widely different types. Hence, it is believed that the results obtained will have general application. Test data on the papers are contained in table 1.

TABLE 1.—*Lithographic-paper test data*[a]

Paper	Weight 25×40: 500	Thickness	Bursting strength	Folding endurance[b]	
				Machine	Cross
	Pounds	*Inch*	*Points*[c]	*Double folds*	*Double folds*
Chemical wood offset paper no. 1	73	0.0054	26	52	10
Rag-content bond	75	.0045	65	1,485	615
Rag chart paper (tub-sized with glue)	125	.0082	95	15,480	8,330

Paper	Degree of sizing (dry indicator method)	Expansion per 15 percent R. H. increase (machine dir.)	Fibers	
			Rag	Chemical wood
	Seconds	*Percent*	*Percent*	*Percent*
Chemical wood offset paper no. 1	45	0.035	----------	100
Rag-content bond	55	.071	85	15
Rag chart paper (tub-sized with glue)	150	.063	100	----------

[a] All tests, except expansion, made by methods of the Technical Association of the Pulp and Paper Industry.
[b] For test specimen 15 mm wide and 90 mm between jaws.
[c] Bursting pressure is lb/in.² through a circular orifice 1.2 inches in diameter.

[2] Weber, BS J. Research 13, 609 (1934) RP730.
[3] Identified as paper no. 1, BS J. Research 13, 609 (1934) RP730.

III. EXPERIMENTAL PRINTING PROCEDURE

The effects of conditioning treatment of paper on the response to offset printing were determined by experimental printings on lots of paper differing only as regards hygrometric condition at the start of the first print. The hygrometric condition was controlled by taking the paper through definite conditioning cycles, and printings were made under controlled conditions of humidity and temperature. The pressroom atmosphere was maintained at 45 $\pm$ 2 percent relative humidity during a part of the study and at 49 $\pm$ 2 percent for the remainder. In the room where the paper was conditioned and stored, a relative humidity 5 to 8 percent above the pressroom condition was maintained after the benefits of this arrangement were indicated in preliminary tests. The conditioning facilities of the National Bureau of Standards were used for preparing many of the papers, and these papers were taken from the Bureau Laboratory to the printing plant in hermetically sealed containers. Each lot of paper treated contained not less than 10 sheets, and the experimental papers were printed with commercial runs. They were placed at the bottom of the pile of paper being printed so as to receive no more than the normal exposure between printings. Papers were not inspected between printings and received no handling, except as part of the commercial run. In some of the work, the corner register marks were "staggered" to facilitate color identification and measurement after multicolor printings. Closeness of register was determined by measuring with a micrometer rule.[4] The center sheets of each lot of paper were used for register measurements and moisture determinations. Printings were made on two presses with similar results. These were Harris, single-color, offset presses of late design, sizes 36 by 48 and 38 by 52. Both presses were in practically new condition. Inasmuch as misregister in the short or around-the-cylinder direction is not generally considered of great importance because it can be corrected by press adjustment, only the long-direction register was studied.

IV. RELATION OF HYGROMETRIC CONDITION OF PAPER TO RESPONSE IN PRINTING

1. VARIATIONS IN MOISTURE CONTENT DURING PRINTING

Papers conditioned to equilibrium with the pressroom air, then printed in 5 to 9 colors, were found to be still approximately in equilibrium but with increased moisture content. The increased moisture content, averaging 0.5 percent, was obviously due to press moisture picked up during printing. The fact that this added moisture could be held while the paper remains in equilibrium indicated that hysteresis was involved, since it is well known that the moisture content of paper under any given conditions may vary by more than 1 percent according to the history of conditioning.[5] This hysteresis effect is illustrated in figure 1, which shows the curves for maximum and minimum moisture contents for a series of offset papers. From a consideration of these data it appeared possible for papers below the maximum curve to increase the equilibrium moisture content; while paper on the maximum curve obviously could not. Hence, it

[4] C. G. Weber and R. M. Cobb. BS J. Research 9, 431 (1932) RP480.
[5] Weber and Snyder, BS J. Research 12, 53 (1934) RP633.

seemed likely that paper conditioned by desorption from an extremely high moisture content to equilibrium with the pressroom atmosphere and printed under constant atmospheric conditions, would not change as long as it remained in equilibrium. In order to try this, papers were preconditioned in humidities considerably higher than that of the pressroom air, then conditioned to equilibrium with the pressroom

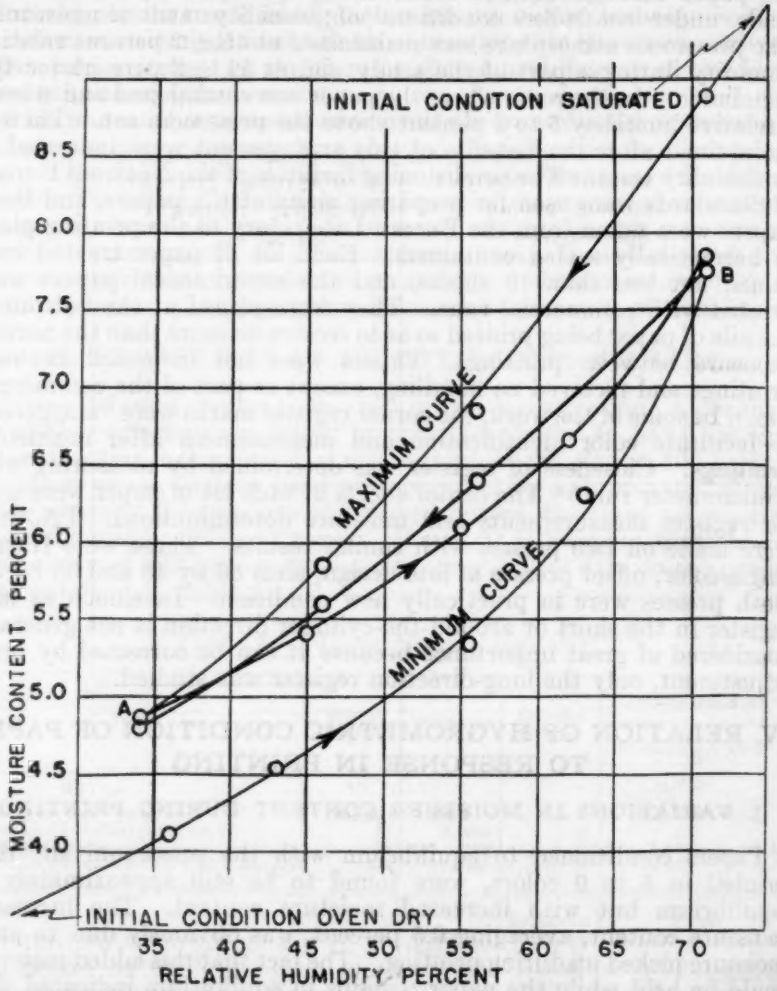

FIGURE 1.—*Equilibrium moisture content of offset papers at different relative humidities*

air and printed. Results of experiments of this kind are shown graphically in figure 2. It will be noted that these papers remained practically constant as regards moisture content during printing. However, this method of conditioning is not feasible for most commercial print shops as it requires two conditioning treatments under widely different atmospheric conditions, and it introduced curling difficulties with the glue-sized paper. Hence, other means of accomplishing similar results were investigated.

Offset papers are normally between the maximum and minimum conditions when received at a print shop, because they must be dried to a moisture content of less than 5 percent in manufacture to permit calendering. To get the moisture content high enough again to place it on the maximum, or desorption, curve after conditioning in the pressroom where 45 to 50 percent relative humidity is commonly maintained, would require putting back 5 percent of moisture, or more. Few mills are equipped to do this, and the moisture content is seldom above equilibrium with 45 or 50 percent relative humidity when received. Such papers gained moisture during printing when conditioned to equilibrium with the pressroom air at the start. There-

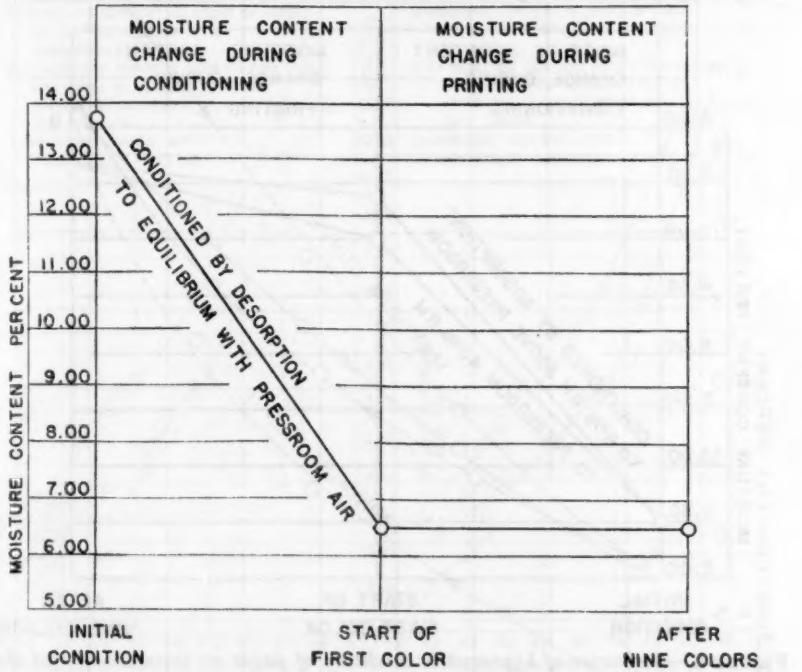

FIGURE 2.—*Influence of hygrometric condition of paper on moisture-content change during multicolor offset printing*

Papers conditioned by desorption.

fore papers were prepared for printing by raising the moisture content above equilibrium with the pressroom air to provide an excess of moisture that might be lost to the air during printing to compensate for the press moisture picked up. These experiments were very successful. It was found that the moisture content of paper conditioned to equilibrium with relative humidity 5 to 8 percent above the pressroom condition remained practically constant during printing. Those conditioned still higher lost some moisture. Typical results showing changes of moisture content during printing are shown in figure 3.

All papers printed reached hygrometric equilibrium with the pressroom air after five or six colors were printed, but never before three

colors were printed. This indicates that the exposure of the paper during printing is sufficient to adjust the moisture content slowly to conform to the room condition. However, it gives no clue as to why the equilibrium moisture content is 0.5 percent higher after printing than before. That is explained, it is believed, by the manner in which the press moisture is applied.

The mutual repellence of greasy ink and water is the basis of lithography. Offset lithography employs a metal plate on which the design is water-repellent and the remainder is grained to hold water. In printing, water is applied to the plate, and it wets all of the plate except the design. Ink is next applied, and it adheres to the design, but is repelled by the wet areas. The image is then

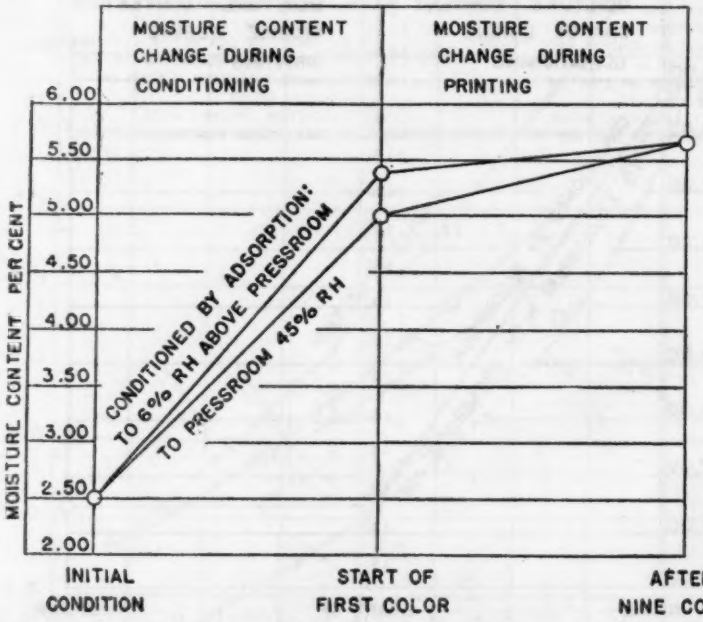

FIGURE 3.—*Influence of hygrometric condition of paper on moisture-content change during multicolor offset printing.*

Papers conditioned by adsorption.

transferred indirectly from the plate to the paper by printing on a rubber blanket from which the actual impression is made. In this operation, water from the wet, nonprinting areas of the plate is transferred to the paper in the same manner that the ink is transferred. Hence, it is likely that the surface of the paper in the wetted areas is at or near the saturation point when the paper goes into the pile on the delivery end of the press. In the pile, the excess moisture can leave the wet areas only by diffusion, and it appears possible that this leaves small portions of the paper with a moisture content equivalent to that on the curve for maximum or desorption moisture content. This may happen with each printing until all of the surface contacting the blanket has been raised to near the condition of maximum moisture content or covered with water-resisting ink. This explanation is shown graphically in figure 4, which shows the minimum or adsorp-

tion and the maximum or desorption curves, and theoretical behavior of moisture content during printing for paper: "A" in equilibrium at the start; "B" conditioned to equilibrium at relative humidity 7 percent above the pressroom condition at start.

It is not probable that A—C and B—C represent the actual paths for total moisture content, but rather the mean between the unmoistened portions of the paper, and the smaller wet portions that follow the path 1—2. The steps in the curves A—C and B—C are based on the fact that, for the papers conditioned to equilibrium with the pressroom at the start, the moisture content increased approximately 0.5 percent during five printings, or an average of 0.1 percent per color. Actually,

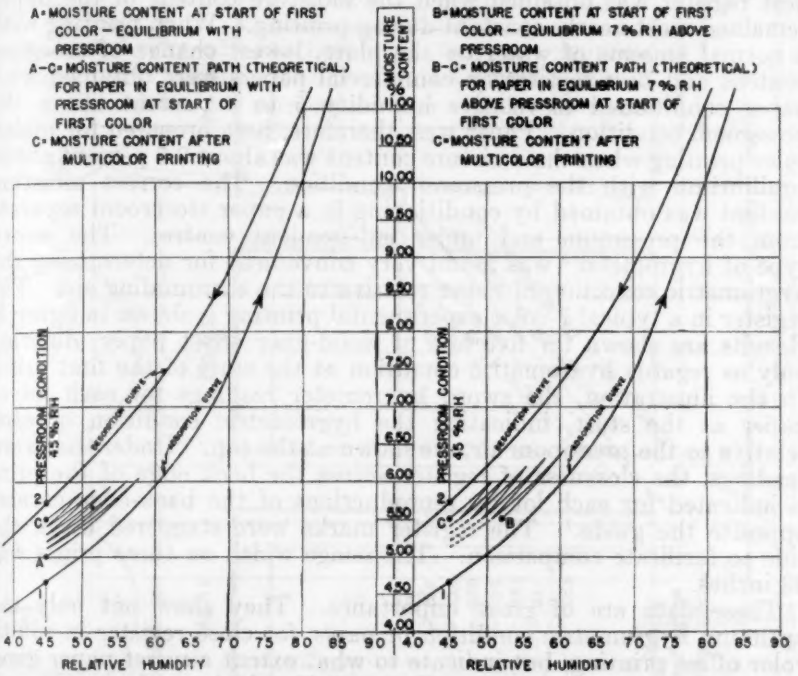

FIGURE 4.—*Moisture-content behavior during multicolor offset printing.*

Minimum or adsorption curves, curves numbered 1, and maximum or desorption curves numbered 2.

the increase was never in equal increments, the greatest increase being for the first colors. The dotted portions of curve B—C represent the probable path if the paper had been exposed sufficiently between printings to come to complete equilibrium with the air. However, the exposure for each color printing is apparently only sufficient for the paper to lose its excess moisture at about the same rate that it takes up press moisture, keeping a balance, when the excess moisture is approximately 0.5 percent at the start.

The validity of the theory that the surface wetting during printing may raise the equilibrium moisture content of paper was checked by laboratory tests. Papers were moistened on one side with a damp sponge; one-half of each lot was conditioned immediately in an atmosphere of 50-percent relative humidity and the other half left in the center of a pile 18 hours and then conditioned. The equilibrium

moisture content for the half left in the pile 18 hours after moistening was higher in every case. The moistening and standing in the pile were analogous to what takes place for each color printing except that more water was applied in the former case.

2. REGISTER OF PRINTS

In all experiments, the register of successive prints was proportioned to the distortion of the paper during printing, and all measurable paper distortion was accompanied by corresponding changes in moisture content. Briefly, the misregister could in all instances be attributed to paper distortion due to gain or loss of moisture. The best register was obtained when the moisture content of the paper remained most nearly constant during printing. When printing with a normal amount of water on the plate, lowest change of moisture content and best register on commercial papers were obtained with paper conditioned to relative humidity 5 to 8 percent above the pressroom condition. Paper was, therefore, best prepared for multicolor printing when the moisture content was about 0.5 percent above equilibrium with the pressroom condition. The correct moisture content was obtained by conditioning in a paper storeroom separate from the pressroom and under independent control. The sword type of hygrometer [6] was found very convenient for determining the hygrometric condition of paper relative to the surrounding air. The register in a typical 7-color experimental printing is shown in figure 5. Results are shown for five lots of wood-fiber offset paper, differing only as regards hygrometric condition at the start of the first print. In the illustration, the sword hygrometer readings for each lot of paper at the start, indicating the hygrometric condition of each relative to the pressroom air, are shown at the top. Under the sword readings, the closeness of register across the back edge of the print is indicated for each lot by reproductions of the back-edge corners opposite the guide.[7] The register marks were staggered down the side to facilitate comparison. The image width on these prints was 43 inches.

These data are of great importance. They show not only the optimum hygrometric condition of paper for close register in multicolor offset printing, but indicate to what extent a moist paper gives better results than a dry one. Paper no. 11, which was in equilibrium at the start, gave no better register than no. 41, which was moist relative to the pressroom air by a sword reading equivalent to 2 percent of moisture content. Paper no. 31, moist by a reading equivalent to 1 percent of moisture, gave much better register than the paper in equilibrium at the start. Optimum results were obtained with papers conditioned to relative humidity 6 to 8 percent above that of the pressroom air, and these papers gave a moist reading on the sword as shown for no. 21 in the illustration. The reading indicates a moisture content approximately 0.5 percent above equilibrium with the air. This conditioning practice has been followed at the Coast and Geodetic Survey on commercial jobs of 9 to 17 colors with most satisfactory results from the start. As compared with the former method of

[6] The Paper Hygroscope, Bulletin of the Lithographic Technical Foundation, New York.

[7] The back-edge corner of a print on the side opposite the guide is the point on the print furthest from all press alignment. Hence, it is the point of maximum lengthwise misregister.

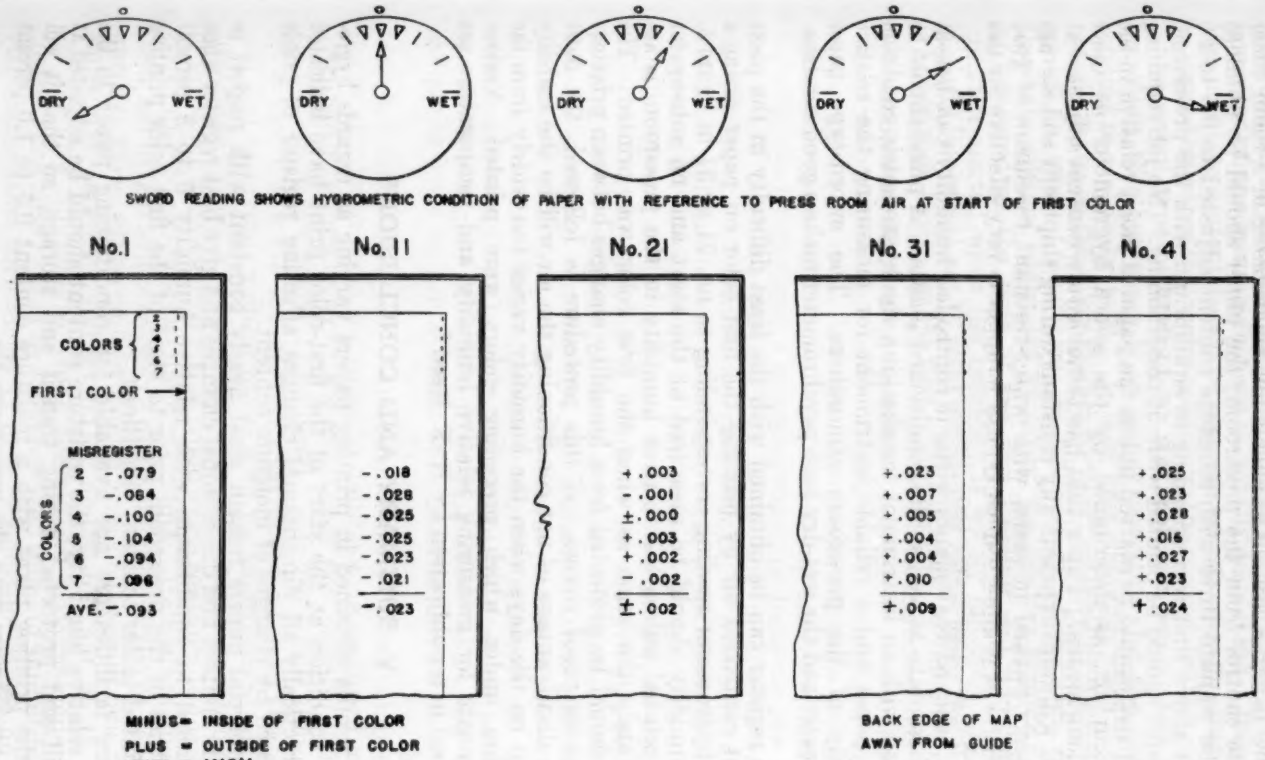

FIGURE 5.—*Relation of paper conditioning to register.*

The sword-hygrometer readings, showing hygrometric condition at the start, are reproduced at the top, and the resultant register for each lot is shown directly underneath. The misregister is shown for the back edge of the map on the side opposite the guide. Plus or minus signs indicate whether the prints are longer or shorter than the first color print. The values given are decimal fractions of an inch.

conditioning to equilibrium with the pressroom, it has resulted in better quality work, decreased spoilage, and higher production.

Where facilities are not available for conditioning in a room under separate control from the pressroom, the paper should be obtained from the manufacturer with moisture content adjusted to 0.5 to 1.0 percent above that corresponding to equilibrium with the pressroom. This paper should be printed without conditioning. No job requiring fine register should be started unless the paper is moist relative to the pressroom air, as determined by the sword hygrometer or other equivalent means. Paper that has the moisture content adjusted at the mill will remain practically constant during shipment and storage if properly packed in cases, with water-resistant caseliners of good quality. The asphalt duplex type of wrapper is very effective for this purpose.

It is believed that plants without controlled humidity can benefit from these data as well as the conditioned plants. A plant should be provided with an instrument for checking the hygrometric condition of the paper and a reliable instrument for measuring the relative humidity of the pressroom atmosphere. The sword-type paper hygrometer and the wet-dry bulb psychrometer make a good combination.

Fine register can be obtained with the least difficulty in the plant without controlled air by printing the first color on paper giving a sword-hygrometer reading corresponding to no. 21 or 31 in figure 5. The humidity should be measured at the start and no subsequent colors printed unless the relative humidity in the pressroom is approximately the same as when the first color was printed. The paper should be protected from humidity changes between printings by moistureproof covers. If this procedure is followed, the most serious disadvantage of not conditioning the air will be the inability to print on the days when the humidity varies too widely from the condition under which preceding colors were printed. Various instruments for measuring relative humidity and temperature are described in a publication by R. F. Reed.[8]

V. SUMMARY AND CONCLUSIONS

The results obtained in printing papers varying as regards hygrometric condition at the start of the first-color print have indicated that practically all dimensional changes affecting register of prints are caused by changes of moisture content.

Commercial papers remain most nearly constant with respect to moisture content and dimensional changes and give best register when conditioned to equilibrium with relative humidity 5 to 8 percent above that of the pressroom prior to start of the first-color printing and printed under constant conditions.

Where facilities are not available for conditioning paper to the higher relative humidity, the moisture content should be adjusted at the mill and protected during transit and storage, so that it will reach the printing plant with a moisture content 0.5 to 1.0 percent above equilibrium with the pressroom air.

[8] Handbook of Air Conditioning for Lithographers, Lithographic Tech. Found., New York.

For the printing plant without controlled humidity, attention to the relationship between moisture content of paper and the relative humidity of the surrounding air is equally important. Paper with high moisture content should be required and no color printing should be started on paper that is dry relative to the surrounding atmosphere.

The sword type of hygrometer is a most convenient tool for determining whether paper is in proper condition for the first-color printing in multicolor work. It is in best condition when the sword reading taken in the pile of paper is "wet" relative to the pressroom air by an amount equivalent to 0.5 percent of moisture content. In plants without controlled humidity, the relative humidity should be measured at the time of the first printing and no subsequent printings started when the humidity is widely different. It is particularly important not to print subsequent colors when the humidity is higher than it was for the first-color printing.

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RESEARCH PAPER RP860

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A SUMMARY OF INFORMATION ON THE PREPARATION AND PROPERTIES OF PURE IRON

By John G. Thompson and Harold E. Cleaves

ABSTRACT

A critical review of available information leads to the conclusion that really pure iron—iron free from significant amounts of all impurities—never has been prepared. Consequently many of the fundamental properties of iron cannot be defined with the accuracy desirable for such an important metal.

Available information on the preparation and properties of the purest available forms of iron is summarized in this paper.

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I. INTRODUCTION

One of the metallurgical researches in progress at the National Bureau of Standards is the determination of the fundamental properties of elemental iron. The extraordinarily important role of the metal, iron, and its alloys in modern industrial life necessitates the acquiring and compiling of adequate and accurate data on this subject. The work is in progress in three stages, (1) the evaluation of existing data, representing the combined efforts in the past of numerous investigators working under a great variety of conditions, by a critical review of the existing scattered information in the technical literature, (2) the preparation in the laboratory of metallic iron of definitely known purity and perhaps of higher purity than has been available heretofore, and (3) the determination of properties of this metal to supplement present available information. The first stage of the project has been completed and the available information from the technical literature is summarized in the present paper.[1] The preparation of high-purity iron is now in progress in the laboratory—the determination of its properties will follow. These phases of the project will be described in subsequent papers.

II. WHAT IS PURE IRON?

The designation "pure iron" has been applied at various times to a variety of ferrous materials. At one time the term connoted either sponge iron, preferably of Swedish origin, or wrought iron; later "pure iron" was used as a synonym for electrolytic iron; at present the term is used in a commercial sense to refer to open-hearth iron despite the fact that carbonyl iron, which is of considerably higher purity, is also available. However, carbonyl iron is not yet comparable to open-hearth iron in the quantity produced nor in price.

In addition to these commercial irons, the technical literature contains many references to laboratory specimens of "pure iron." Analyses of these were seldom made, however, partly from disinclination to sacrifice a large portion of the material for analytical samples and also because the precautions observed in the preparation were assumed to insure the purity of the product.

Much of the confusion as to what constitutes "pure iron" can be attributed to the changing opinion regarding pure metals in general. From earliest times, the common metals have been produced by smelting processes. The metal produced by smelting is always contaminated in some degree, by impurities either in the ore or introduced during the smelting operation. The degree of purification varies widely; gold of high purity can be produced by pyrometallurgical processes relatively easily, but the difficulties are intensified in the case of iron by the high temperatures required for smelting and the great affinity of molten iron for elements such as carbon, silicon, manganese, sulphur, and phosphorus. The presence of certain impurities in most metals was formerly considered unavoidable and therefore unimportant, but recently there has been an increasing apprecia-

[1] The review of available information from the technical literature is presented in more detail in the recently published volume, The Metal—Iron. This is one of the series of monographs which, when completed, will constitute a complete and critical review of available information in regard to iron and its important alloys. The series of monographs is being published by the Iron Alloys Committee of the Engineering Foundation; The Metal—Iron is a contribution of the National Bureau of Standards to the program of the Iron Alloys Committee.

tion of the marked effect of very small amounts of impurities and minor constituents on the properties of metals.

Recognition of this importance in the case of iron undoubtedly has been delayed by the fact that the properties such as strength, hardness and magnetic properties of slightly contaminated iron are superior to those of commercially pure metal. Only recently, in attempts to determine the fundamental properties of iron, particularly the magnetic properties, has it been shown that apparently insignificant amounts of impurities such as carbon, oxygen and sulphur may be of considerable importance. Cioffi (57) [2] reported that the sulphur absorbed at 1,300° C from an atmosphere containing 0.05 percent of hydrogen sulphide reduced the permeability of iron to less than one-third of its initial value. Still more striking is the conclusion of Yensen and Ziegler (72) that the presence of 0.002 percent of carbon reduced the maximum permeability of iron to approximately one-half that of the carbon-free metal. They found also that the first traces of oxygen exert a pronounced effect on the permeability although oxygen is about one-fifth as potent as carbon in this respect; an oxygen content of 0.01 percent reduced the permeability by approximately 50 percent.

It is evident on the basis of such data that the use of the adjective "pure" should be limited to metal that is known to be free from all impurities, in other words, to metal that approaches "elemental" iron in purity. From this point of view, pure iron is an unattained ideal; the best accomplishment to date is *high-purity* iron, not *pure* iron.

III. HIGH-PURITY IRON

Iron which may be classed as of high purity has been prepared by a number of investigators. However, the purity can seldom be stated with exactness; only recently has the need for complete analyses of extreme accuracy been recognized. Such analyses are difficult and entirely satisfactory methods are not always available. Since the applicability of chemical analysis is limited by the purity of available reagents, reliable results can be obtained only when the constituent to be determined is present in an appreciably greater amount than the blank correction which must be applied. For example, the determination of carbon in an amount of the order of 0.002 percent is extremely difficult with available methods, yet this amount of carbon is decidedly significant in its effect on the magnetic properties of iron. Spectrochemical analysis for the detection of important elements such as carbon, oxygen, and sulphur, to which the spectroscope is relatively insensitive, is very difficult and of doubtful value. Determinations of certain properties, magnetic, thermal, or electrical, have been proposed as criteria of purity but, as yet, the proposed methods of this kind have not been satisfactorily developed. An entirely reliable method for determining the degree of purity of high-purity iron still remains to be developed. The lack of accurate information on the composition of various high-purity irons from different sources or prepared by different methods renders their comparison extremely difficult.

[2] The figures in parentheses here and throughout the text refer to the list of selected references at the end of the paper.

1. BASIC OPEN-HEARTH IRON

The one type of high-purity iron for which extended commercial application has been found is open-hearth iron. The composition of Standard Sample 55 of the National Bureau of Standards, representing open-hearth iron, is shown in table 1. The presence of so many elements in determinable amounts is evidence of unusual care and completeness in the analysis rather than of impurity of this particular specimen. Several of the elements reported are not ordinarily determined in the analysis of ferrous materials. Open-hearth iron of this degree of purity, roughly 99.85 percent of iron, is the optimum result obtained to date by pyrometallurgical methods. Corresponding information on charcoal irons and sponge irons is not available. However, the incomplete analyses which are available indicate that the purity of the products analyzed, aside from occluded slag particles, was somewhat less than that of open-hearth iron.

TABLE 1—*Composition of basic open-hearth iron*

[National Bureau of Standards Standard Sample 55]

Element	Percentage
Oxygen	0.07
Copper	.041
Nickel	.020
Manganese	.019
Sulphur	.017
Carbon	.013
Arsenic	.012
Tin	.008
Cobalt	.006
Nitrogen	.004
Phosphorus	.003
Chromium	.002
Molybdenum	.002
Aluminum	.002
Antimony	.002
Silicon	.001
Total of impurities determined	0.222

2. ELECTROLYTIC IRON

Electrolytic iron has been produced in a number of processes varying widely in aim and scope of operation and in detail. Much of this work was done before the importance of very complete analyses was recognized, consequently the available analyses are in general decidedly incomplete. Cain, Schramm, and Cleaves (10) were the first to report nickel and cobalt, now recognized as major impurities in most electrolytic irons. Recent reports (53, 59) from the National Physical Laboratory in England, where the production of very pure iron has been under investigation for a number of years, state that metal containing 0.033 percent of impurities (0.022 percent of nickel, 0.006 percent of carbon, 0.003 percent of chromium, 0.001 percent of phosphorus, 0.0008 percent of copper, 0.0005 percent of silicon, and no sulphur or manganese, with no mention of oxygen) is considered to be about the best obtainable by electrodeposition. Electrolytic iron of this composition is of somewhat higher purity than the earlier electrolytic irons, although a review of the incomplete analyses

reported in the literature indicates that the total of impurities in hydrogen-free electrolytic irons of good quality was consistently less than 0.1 percent. The purity of electrolytic iron by difference is assumed to be 99.9 percent or above, a value somewhat superior to that of open-hearth iron.

3. LABORATORY IRONS

Many attempts have been made to produce small amounts of extremely pure iron by careful purification of a compound of iron with subsequent reduction to metal. The two specimens which probably represent the purest iron ever produced were prepared by laboratory methods. These are the irons prepared about 1910 by Lambert and Thomson (2) for studies of the theory of corrosion, and by Baxter and Hoover (3) about 1912 for a determination of the atomic weight of iron, which is accepted as one of the best ever made. Both processes consisted essentially in elaborate purification of ferric nitrate, conversion of this compound to oxide, and reduction by means of purified hydrogen. Results of analyses of the irons were not reported and belief in their high purity is based on the precautions observed in the preparation and on the properties exhibited by the metal.

Much of the difficulty encountered in the application of these laboratory methods occurs in the reduction of the purified compound and in the melting of the resulting metal. Because of this the Physikalisch-Technische Reichsanstalt (1) in 1909 concluded that electrolytic methods were preferable to laboratory methods as a practical means of producing high-purity iron; on the other hand, according to recent reports (53, 59) the opposite conclusion has been reached by the National Physical Laboratory. The National Bureau of Standards has adopted a method similar to that of Lambert and Thomson or of Baxter and Hoover, but operated on a larger scale, as the most promising for the production of iron of really high purity.

4. OTHER HIGH-PURITY IRONS

Carbonyl iron, prepared in Germany according to processes described by deLangeron (26), Mittasch (34), Pincass (38), and Winter (51), has recently become available in quantity. It has been claimed that this iron is substantially free from all impurities except carbon and oxygen; other elements being absent either because they do not form volatile compounds or because their volatile compounds, if present, do not decompose under the conditions which obtain in the decomposition of iron carbonyl. Recent examination, at the National Bureau of Standards, of a few selected specimens of carbonyl iron showed that these specimens contained small but determinable amounts of several metallic elements as well as of nonmetallic constituents, but nevertheless were of high purity. Oxygen was not determined in these samples; the total of the impurities determined was roughly 0.015 percent in each case. These analyses are substantiated by the data given by Wells, Ackley, and Mehl (70), but additional evidence is desired to establish fully the purity and uniformity of carbonyl iron.

Sublimation processes are applicable for the purification of certain metals such as magnesium and manganese, but, according to Kroll (63), not for the preparation of pure iron.

Maintaining solid iron in an atmosphere of purified hydrogen at a high temperature for a prolonged period has been used to reduce the carbon, sulphur, oxygen, phosphorus and nitrogen contents. Metallic impurities are not reduced in amount by this treatment. Iron treated in this manner exhibits superior magnetic properties as stated by Cioffi (58) and others.

In the study of pure iron, if it is ever obtained, it will be desirable to use single-crystal specimens for the determination of certain properties. The most successful method for the production of large crystals of iron is the "strain-anneal" method used by Edwards and Pfeil (17). While this method was successful with small flat specimens of iron of only fair purity, subsequent attempts by Gries and Esser (36) and by Ziegler (42) with larger specimens of vacuum-melted electrolytic iron were not entirely successful.

5. SUMMARY OF THE METHODS OF PREPARATION OF HIGH-PURITY IRON

The purest irons ever produced are believed to be those prepared by Lambert and Thomson and by Baxter and Hoover by small-scale laboratory operations. However, the high degree of purity of these specimens is an assumption based on the method of preparation, precautions taken, and properties of the metal; analyses of the products were not reported. Available information indicates that the best electrolytic iron contained less than 0.1 percent total of impurities, electrolytic iron thus being slightly superior in purity to open-hearth iron. The degree of purity of carbonyl iron is very high but has not been definitely established.

IV. PROPERTIES OF IRON

Since pure iron has never been prepared in useful quantities, its fundamental properties have not been directly determined. Likewise, the purest irons that have been prepared have been available in amounts too small to permit the determination of many properties. The following summary of the best available information on the properties of pure iron, in some instances is based on specimens of electrolytic iron; in some instances available information is limited to the properties of basic open-hearth iron.

1. ATOMIC PROPERTIES

Iron is number 26 in the periodic table of the elements and is placed in the eighth group associated with cobalt and nickel.

Its atomic weight is 55.84 (56). Aston (48) has concluded that there are two isotopes of mass 56 and 54, respectively, the latter being about 5 percent as abundant as the principal isotope.[3]

Iron forms two series of chemical compounds, ferrous and ferric, in which the iron is bivalent and trivalent, respectively.

2. ALLOTROPY

X-ray studies have established the existence of three allotropic modifications of solid iron, each being stable within a definite temperature range; alpha iron at ordinary temperatures, gamma at intermediate temperatures, and delta at temperatures which approach the melting point.

[3] In a recent article, Proc. Roy. Soc. (London) 149, 396 (1935), Aston identified a third isotope of mass 57, about 3 percent as abundant as the principal isotope.

The change of the alpha allotrope to the gamma form and vice versa, which was termed the A_3 transformation by Osmond in 1890, was formerly believed to occur over a rather wide range of temperature because the transformation on heating, Ac_3, was observed at a higher temperature than the reverse change, Ar_3, on cooling. It has now been established that the divergence between these two observed temperatures can be attributed to two factors, too rapid a rate of heating or cooling and the presence of impurities in the iron. Both of these factors affect the Ar_3 temperature more than they do the Ac_3 temperature. Recent work with samples of high-purity iron heated and cooled at very slow rates has shown that the Ac_3 and Ar_3 temperatures coincide within the limits of experimental error. A critical review of available information has established the most probable value for the temperature of the A_3 transformation as 910° C (1,670° F). Data have been published indicating that A_3 in very pure iron occurs at a temperature appreciably higher than 910° C, but according to a recent announcement the high value, 930° C, obtained in one of these investigations was affected by an unsuspected pyrometric error. Correction for tnis error gave a value for A_3 close to 910° C. Furthermore, Wells, Ackley, and Mehl (70) recently showed that several samples of the purest iron available all transformed at 910° C. Accurate knowledge of the temperature of the A_3 transformation, of course, forms the fundamental basis of the heat treatment of ferrous metals.

At 1,400° C (2,550° F), the A_4 transformation, the gamma allotrope changes to the delta form, which is stable at all temperatures up to the melting point.

In addition to the allotropic transformations at 910 and 1,400° C, there is an important change in the magnetic properties of iron at about 770° C, the A_2 point. This change from ferromagnetic to paramagnetic iron is a reversible one like the allotropic transformations but, since no change in crystalline structure occurs, both ferromagnetic and paramagnetic iron being the alpha allotrope, this change is called a magnetic transition, not a transformation.

Suggested additional transformations at temperatures other than A_3 and A_4, based on observed irregularities in the properties of iron, have not been confirmed by X-ray studies, and some of the irregularities have been definitely associated with the presence of impurities. According to Heindlhofer (61) no allotropic change in iron below 0° C has ever been observed.

3. STRUCTURE

Crystallographic studies of iron crystals indicated that iron crystallizes in the cubic or isometric system. X-ray studies have confirmed this and in addition established the atomic arrangement of alpha iron as body-centered cubic, the lattice constant being 2.861 angstrom units at 20° C and about 2.90 just below the A_3 temperature.

X-ray studies at temperatures above A_3 have shown that gamma iron has a face-centered cubic structure and that at temperatures above A_4 delta iron has a body-centered cubic structure like alpha iron. The A_3 change is accompanied by an increase in the lattice constant, from about 2.90 angstrom units for alpha iron to about 3.64 for gamma iron. With increasing temperature the lattice

constant of gamma iron increases, the value being about 3.68 angstrom units at the A_4 point. The lattice constant of delta iron is about 2.92, this value agreeing approximately with an extrapolation from data on the effect of temperature on the lattice constant of alpha iron.

The normal microstructure of alpha iron, or ferrite, is that characteristic of pure metals in general—allotriomorphic crystalline grains. Various unusual features such as a fibrous, columnar, conical, or broken structure have been observed in electrolytic iron, as deposited, but investigations such as that of Blum and Rawdon (15) have shown that these are determined primarily by the conditions of electrodeposition. They are not inherent characteristics of the metal. Remelted electrolytic iron has a microstructure comparable to that of ferrite from other sources.

Certain unusual features termed veining or network structures have been observed (28, 35) within the ferrite grains examined under ordinary conditions. Alpha veining, an indistinct "phantom" network superimposed upon the ordinary alpha structural pattern, is a common occurrence in electrolytic and open-hearth iron and is generally considered to be associated with the fact that the metal has undergone the alpha-gamma transformation. However, some observers (65) believe that the presence of impurities is primarily responsible for alpha veining. A network pattern which appears to be associated with the previous existence of the metal in the gamma and delta states also has been observed in etched ferrite grains. Examples of these various structural features are shown in figure 1. The effect of these features on the mechanical properties is believed to be insignificant.

Twinning occurs readily in coarse-grained open-hearth iron deformed by impact, but only occasionally in purer forms of iron.

The microstructure of iron can also be revealed by heat-etching, i. e., if a polished specimen is heated in an evacuated chamber at a high temperature, slight volatilization occurs, this being somewhat greater at the grain boundaries so that an outline of the crystal pattern is formed. The effect is sometimes intensified by the volume change which accompanies the A_3 transformation, a slight "buckling" of the surface being the visible result.

A Widmanstätten or martensitic structural pattern can be developed in basic open-hearth iron by quenching from about 1,400° C, but the development of these structures is apparently dependent on the presence of a small amount of carbon. Tritton (30) could not produce this feature in low-carbon electrolytic iron and in the recent work of Mehl and Smith (64) with electrolytic iron, success in its development was reported to be sporadic and unpredictable.

4. DENSITY

Values of the density of iron have been obtained by direct determination with specimens of the highest purity obtainable, by extrapolation to zero impurities of results obtained from a series of irons or alloys, and by calculation based upon determinations of the lattice constant. The results of the best determinations by all three methods are in good agreement and indicate that 7.87 g/cm^3 is the best present approximation for the density of pure iron.

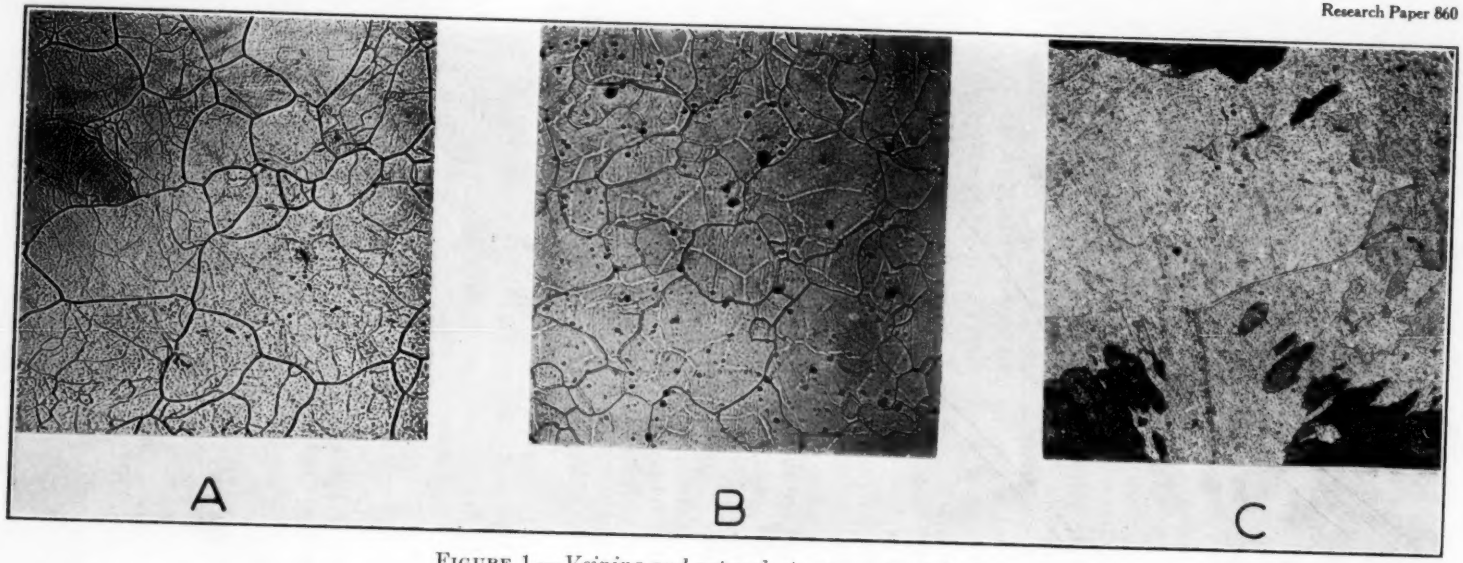

FIGURE 1.—*Veining and network structures in alpha iron.*

A. Alpha veining in electrolytic iron. × 100. B. Gamma network in ferrite grains. × 100. C. Delta network in ferrite grains. × 50. [Rawdon and Berglund (*28*).]

5. COMPRESSIBILITY

Bridgman (12) found that the mean value for the cubic compressibility of open-hearth (Armco) iron, for pressures between 0 and 10,000 kg/cm², was 0.566×10^{-6}/kg/cm² at 30° C and 0.572×10^{-6} at 75° C. Unpublished data obtained by Dr. L. H. Adams of the Geophysical Laboratory, Carnegie Institution of Washington, showed the compressibility of a sample of high-purity iron to be the same, within 1 part in 500, as that of a sample of Bessemer steel. Evidently compressibility is not greatly affected by minor changes in composition.

6. MELTING POINT AND HEAT OF FUSION

The melting points of several metals have been determined with sufficient accuracy so that they are used as fixed points on the pyrometric scale, but this applies to metals which are readily obtained in states of higher purity than has been possible for iron. The difficulty of obtaining high-purity iron, the lack of accurate information regarding the purity of the samples used for melting-point determinations, and the difficulties in pyrometric observations at temperatures of 1,500° C, or higher, all help to account for the lack of agreement in the results obtained in different determinations of the melting point of iron.

Eight published values have been selected as being the best with respect both to purity of material and to pyrometric procedure. Corrections of some of these values are necessary, however, on account of changes in the pyrometric scale and in radiation formulas, which have been made since the determinations were reported. These corrected values range from 1,527° C, reported by Jenkins and Gayler (40), to 1,537° C, reported by Burgess and Waltenberg (6). The numerical average of the eight values is 1,534° C, which is rounded to 1,535° C (2,795° F) as the best present approximation of the melting point of iron.

A review of the diversified values obtained by different investigators suggests the rounded value 65 cal/g or 3,630 cal/g-atom as the best present approximation for the heat of fusion of iron.

7. BOILING POINT AND HEAT OF VAPORIZATION

The boiling point of iron is so high that direct determinations are not practicable; the method most frequently employed is extrapolation of data for the vapor pressure of molten iron at various temperatures. The rounded value 3,000° C (5,430° F) defines the probable boiling point of iron as closely as the data warrant.

From thermodynamic consideration of thermal data, Kelley (68) calculated that the heat of vaporization of iron at the boiling point is 1,515 cal/g or 84,620 cal/g-atom. However, 2,735° C was used as the boiling point of iron, a value which is considerably lower than the selected value of 3,000° C.

8. MECHANICAL PROPERTIES

(a) TENSILE PROPERTIES

Freshly deposited electrolytic iron may possess a tensile and a yield strength of more than 100,000 lb/in.², with an elongation as small as 3 percent (gage length not given). For the same material

in the annealed condition, tensile strength between 40,000 and 55,000 lb/in.^{2}, yield strength between 20,000 and 25,000 lb/in.^{2}, and elongation between 25 and 45 percent (gage length usually about 2 in.), have been reported. Such values are roughly comparable with those obtained with open-hearth (Armco) iron. Fusion in vacuum with subsequent annealing further softens electrolytic iron. The reported properties of such material are: tensile strength between 35,000 and 40,000 lb/in.^{2}, yield strength between 10,000 and 20,000 lb/in.^{2}, elongation of 30 to 60 percent in a gage length of 1.5 in., and reduction of area between 70 and 90 percent.

The tensile strength of electrolytic iron decreases with increasing testing temperature up to about 100° C, then rises to a maximum at about 250° C, and decreases with further increase in temperature. The temperature of maximum strength in electrolytic iron is somewhat lower than the "blue-heat" range of commercial steels. The

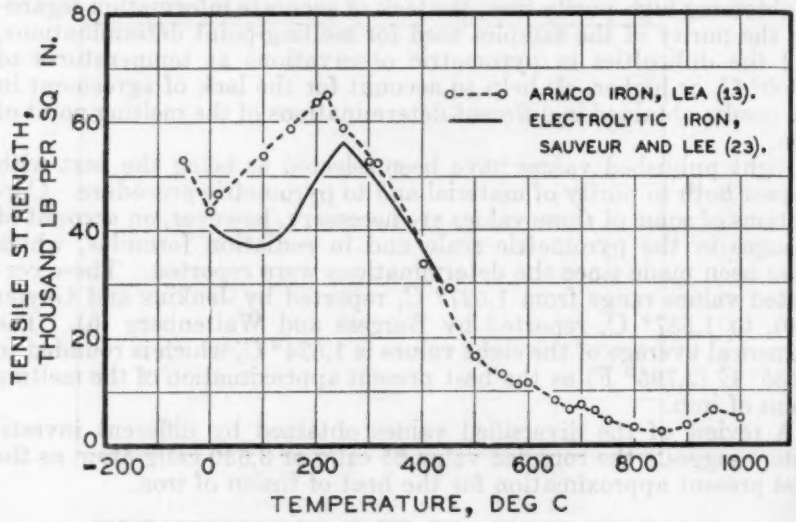

FIGURE 2.—*Tensile strength of open-hearth (Armco) iron and of electrolytic iron at various temperatures.*

effect of increasing temperature on the tensile strength of electrolytic and of open-hearth irons is shown in figure 2.

Tensile properties of single-crystal specimens have been reported only for material which approximated the composition of Armco iron, for which tensile strengths of 20,000 to 35,000 lb/in.^{2}, yield strengths of 4,000 to 9,000 lb/in.^{2}, and elongations for 1-in. gage length of 30 to 85 percent were obtained.

(b) ELASTIC PROPERTIES

Abram (52) concluded that Young's modulus of pure iron in the annealed condition should be about 30,000,000 lb/in^2. The elastic moduli of single-crystal specimens of iron vary in the direction of different crystallographic axes (62). Goens and Schmid (46) reported that Young's modulus in a single crystal of open-hearth (Armco) iron was 19,000,000 lb/in.^{2} in the direction of the cube axis (the [100] direction) and 41,000,000 lb/in.^{2} in the direction of the cube diagonal (the [111] direction).

The modulus of elasticity of open-hearth (Armco) iron decreases as the temperature increases up to about 500° C (13, 29).

(c) HARDNESS

Brinell numbers as low as 50 for fully annealed electrolytic iron, and as high as 360 for freshly deposited metal, have been reported. Brinell numbers between 60 and 70 are frequently reported for vacuum-melted electrolytic iron as well as for other forms of high-purity iron and for open-hearth iron in the annealed condition. The Brinell number of electrolytic iron can be increased to about 200 by cold work (27), but the rate of increase is not so rapid for electrolytic iron as for open-hearth steel (21).

The Brinell number of iron is not appreciably affected by variation in grain size and, in single-crystal specimens subjected to cold rolling, there is no very significant difference in the ball-indentation hardness of different crystallographic faces, as shown in figure 3. However,

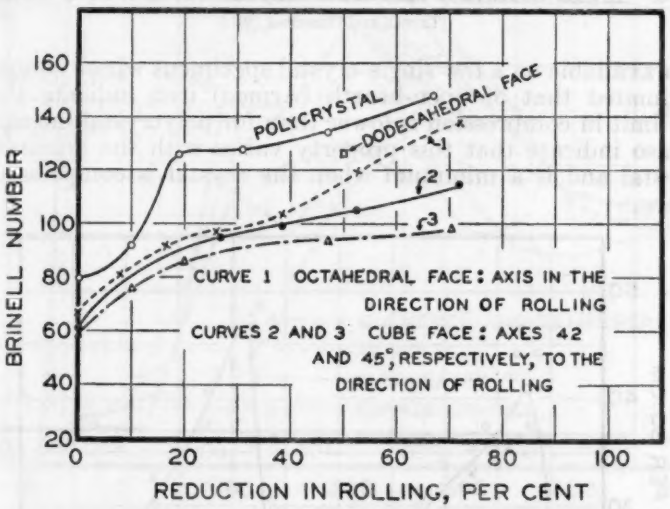

FIGURE 3.—*Variation of hardness with degree of rolling of polycrystalline iron and of single-crystal specimens with different orientation.*
[Gries and Esser (32).]

there appears to be a difference in the rate of work hardening in different crystallographic directions.

With a slight increase in the testing temperature the hardness of fairly pure iron is decreased slightly. Further increase in temperature is accompanied by an increase in hardness, which reaches a maximum at about 200° C; above this point increases in temperature result in a progressive decrease in hardness, figure 4. On the other hand, according to O'Neill (37), determinations of scratch hardness show a continual decrease in hardness with increasing temperature.

(d) STRENGTH IN COMPRESSION

The properties of open-hearth (Armco) iron in compression according to Moore and Kommers (11) are as follows:

Elastic limit	19, 400 lb/in.²
Proportional limit	19, 200 lb/in.²
Yield strength	20, 600 lb/in.²

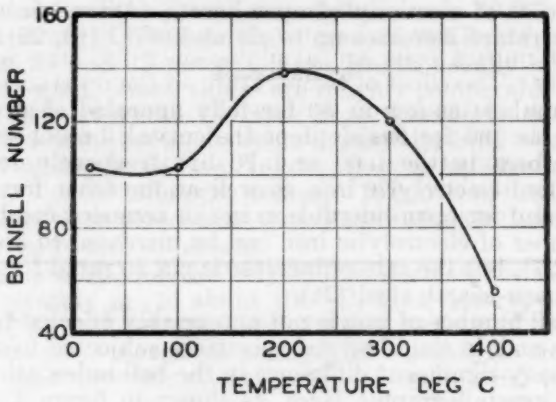

FIGURE 4.—*Brinell numbers of open-hearth (Armco) iron at various temperatures.*
[Tapsell and Clenshaw (29).]

Data available on a few single-crystal specimens whose composition approximated that of open-hearth (Armco) iron indicate that the elastic limit in compression is lower than for polycrystalline material. They also indicate that this property varies with the orientation of the crystal and is a minimum when the crystal is compressed on a cube face.

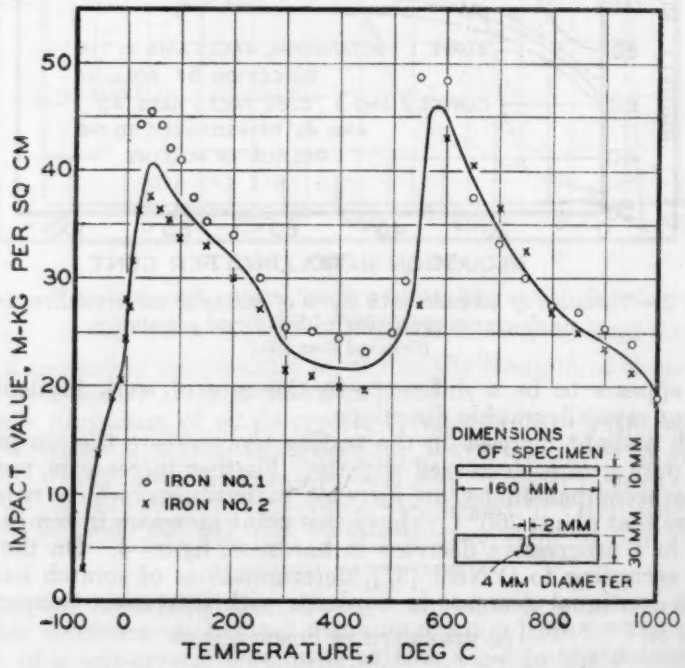

FIGURE 5.—*Results of impact tests on open-hearth iron.*
[Goerens and Hartel (4).]

(e) RESISTANCE TO IMPACT

Results of impact tests are available only for material of commercial purity. The effect of temperature on the resistance to impact of open-hearth (Armco) iron is shown in figure 5. The significant features are the precipitous slope of the curve at room temperature and the two maxima, the first one only slightly above room temperature, the other at about 600° C. The position of the first maximum can be varied over a considerable range of temperature by varying

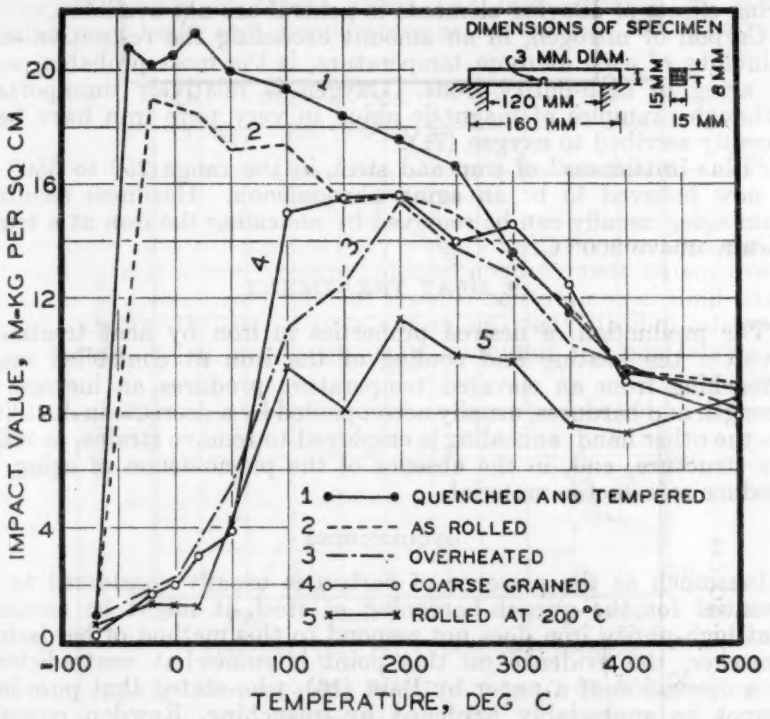

FIGURE 6.—*Effect of previous thermal and mechanical treatment on the notch brittleness of open-hearth iron.*

[Körber and Pomp (22).]

the thermal and mechanical treatment of the specimens, as shown in figure 6. The variable results obtained in impact tests of open-hearth (Armco) iron at room temperature can be largely attributed to the sensitivity of the impact resistance to slight changes in temperature and to the known effects of size and type of specimens.

(f) ENDURANCE

Reported results for the endurance limit of open-hearth (Armco) iron, which are the only available data on the fatigue of iron, range from 12,000 to 38,000 lb/in.^{2}, the variations in conditions of test and the size and previous history of the specimen being responsible for the lack of precision. Values between 24,000 and 28,000 lb/in.^{2} have frequently been reported.

(g) EFFECT OF AGING

Since the phenomenon of aging, or change in the properties of metals with time, is associated with the presence of minor constituents or impurities, aging effects would be expected to decrease in magnitude with increasing purity of the material. Aging has not been observed in vacuum-melted electrolytic iron, but does occur in iron of commercial purity as a result of the presence of carbon, nitrogen, or copper (43). Aging has been observed to result from the presence of beryllium or tungsten in steel, but complete data on the aging effects of alloying elements in general are not available.

Carbon or nitrogen, in an amount exceeding the respective solid solubility of each at room temperature, is the most probable cause of aging in high-purity irons. Oxygen is relatively unimportant although examples of magnetic aging in very pure iron have been recently ascribed to oxygen (71).

"Blue brittleness" of iron and steel, in the range 250 to 350° C, is now believed to be an aging phenomenon. Hardness resulting from aging usually can be removed by annealing the iron at a temperature above 200° C.

9. HEAT TREATMENT

The production of desired properties in iron by heat treatment involves the heating and cooling of the iron at controlled rates. Quenching from an elevated temperature produces an increase in strength and hardness, usually accompanied by a decrease in ductility. On the other hand, annealing is employed to remove strains, to refine the structure, and, in the absence of the phenomenon of aging, to produce soft ductile material.

(a) QUENCHING

Inasmuch as the presence of carbon is usually considered to be essential for the quench-hardening of steel, it might be assumed that high-purity iron does not respond to this method of hardening. However, the evidence on this point is somewhat contradictory. In a discussion of a paper by Bain (16), who stated that pure iron cannot be appreciably hardened by quenching, Rawdon reported that small areas on a specimen of electrolytic iron, containing 0.02 percent of carbon, had been decidedly hardened by heating in air with a high-potential spark, with subsequent cooling at an extremely rapid rate. A Widmanstätten or martensitic structure was developed by Sauveur and Chou (39) in electrolytic iron by drastic quenching from above A_3, and Mehl and Smith (64) found that a similar structure could occasionally be obtained in quenched electrolytic iron which contained only 0.004 percent of carbon.

Kenyon (33) has shown that a Brinell number of 110 was obtained for basic open-hearth iron quenched in water from 940° C after hot rolling, whereas a Brinell number of about 80 is characteristic of the same material annealed at 900° C and slowly cooled.

(b) ANNEALING

Freshly deposited electrolytic iron contains relatively large amounts of hydrogen and is brittle. Annealing at any temperature above room temperature reduces the hydrogen content and the hardness,

but the maximum results are obtained only by heating above A_3, as is shown in figure 7. Likewise, the effects of cold working are only partially removed by heating to 500 or 600° C, as is shown in figure 8; complete recovery of the cold-worked metal requires annealing at temperatures of at least 800° C.

The microstructure of cathode electrolytic iron is not greatly affected by annealing unless the temperature is above A_3, under which condition the structure changes rapidly to that of allotriomorphic grains characteristic of ordinary ferrite.

Recrystallization of ferrite which has been strained by cold-working may begin at a temperature as low as 400° C. The rate

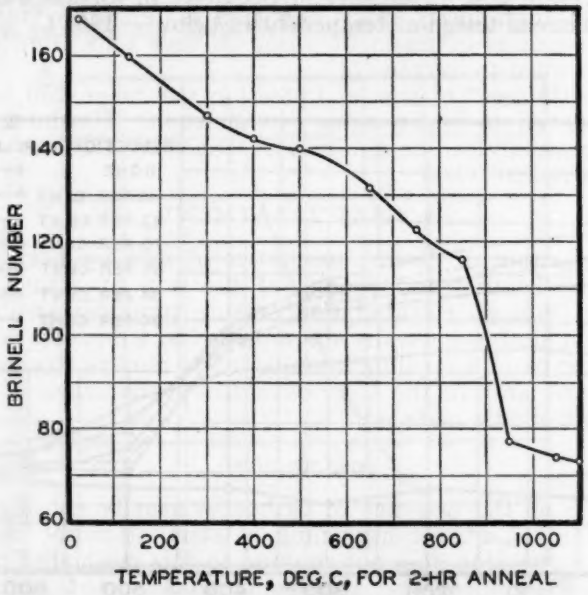

FIGURE 7.—*Effect of annealing on the Brinell hardness of cathode electrolytic iron.*
[Cazaud and Hugues (20).]

of recrystallization increases slowly with increase of temperature up to about 700° C and more rapidly from 700° C to the A_3 point. Annealing characteristics depend upon the extent of the previous cold-work.

The strain-anneal method for the production of abnormally large crystals or of monocrystalline specimens appears to be practicable for iron of commercial purity, but of doubtful merit for purer forms of iron. Oberhoffer and his associates (14) found that maximum grain growth in commercial iron appeared after 10-percent deformation followed by annealing at 700 to 800° C, but could not establish (18) the corresponding conditions for electrolytic iron, although Stead and Carpenter (5) had previously reported a change of this kind in cold-worked electrolytic iron, after heating for a short time at a temperature slightly above A_3, followed by slow cooling to room temperature. However, abnormally large crystals were obtained only in thin sheets of electrolytic iron, about 0.01 in. in thickness.

Impurities present in commercial irons appear to facilitate the production of very large crystals.

10. PLASTIC DEFORMATION

The capacity of iron for plastic deformation and the ease with which deformation may be accomplished, increase with increasing temperature for each of the allotropic forms. The disappearance of plasticity at very low temperature was studied by Heindlhofer (61), who concluded that different tests, such as torsion, impact, and tensile tests, involve different combinations of stresses and, consequently, the relation between temperature and plasticity varies with the type of test. Evidence of plasticity in torsion was lacking only in specimens tested at temperatures below −190° C.

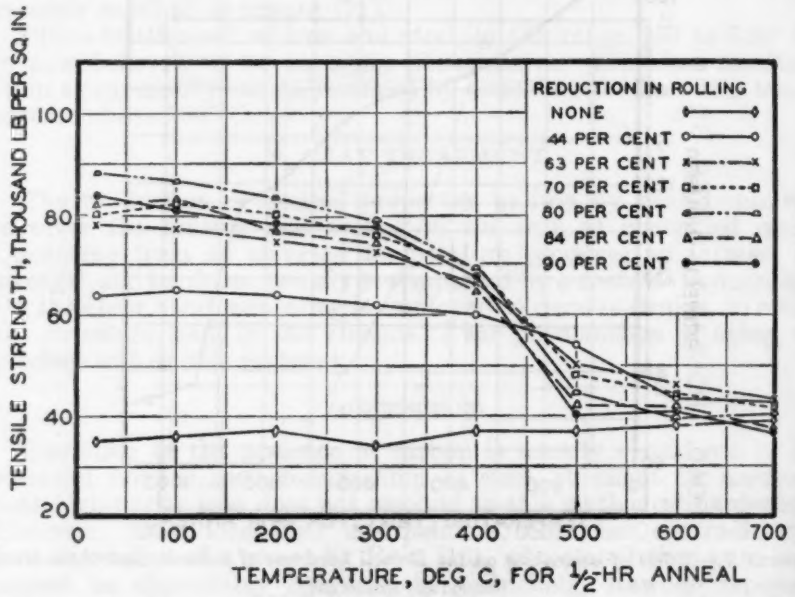

FIGURE 8.—*Effect of annealing on the tensile strength of cold-rolled electrolytic iron.*
[Freeman (24).]

The first visible evidence of plastic deformation of iron stressed in tension at ordinary temperature is the macroscopic surface condition known as Piobert or Lüders lines, "worms", or "stretcher strains." Microscopical examination shows evidence within many of the grains of deformation by slip. With increasing deformation, the grains in which slip bands occur increase in number and the directions of slip within the various individual grains no longer indicate a general prevailing direction of deformation. With greater deformation the grains become elongated and otherwise distorted. The mechanism of the first stages of plastic deformation has been extensively investigated. Most recent investigators agree with Mathewson (49) in the theoretical conclusion that plastic deformation of an iron crystal occurs in the direction of a line of closest atom packing by block movement on planes of the densest atom packing. Difficulty is experienced in

determining the orientation of the slip planes, according to Mathewson, because of the tendency toward rotation which accompanies block movement in a crystal under stress, with consequent increase of stress in other eligible slipping directions. In ordinary polycrystalline material the process is further complicated by inhomogeneity of the force field at the grain boundaries.

The decreased elastic limit of iron with increasing temperature and the increased atomic mobility which tends to decrease or to prevent work hardening in the material, are reflected in the increased ease and capacity for plastic deformation in iron with increasing temperature. Marked changes in the deformation characteristics occur at the temperatures of the allotropic transformations and irregularities also may be due to solubility phenomena of alloying elements or impurities, particularly those present as intergranular material.

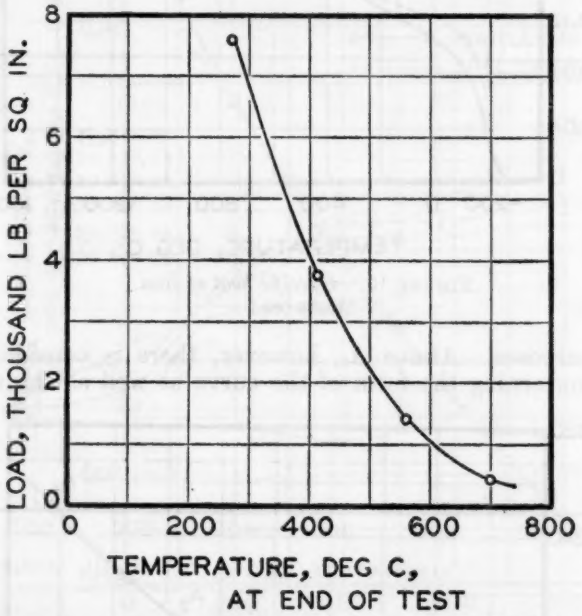

FIGURE 9.—*Stress-temperature relation in iron after 150-hour tests.*
[Austin and Gier (54).]

The recent recognition of the importance of the time factor in the plastic deformation of iron has led to the development of a variety of "creep tests", mostly conducted at elevated temperatures and on structural metals. One of the few studies of the "creep" of high-purity iron is that of Austin and Gier (54) of the applicability of the Rohn method of test. Figure 9 shows how the load-carrying capacity decreases with increasing temperature in this test.

11. THERMAL PROPERTIES

(a) SPECIFIC HEAT

Available information on the specific heat of iron at various temperatures has been summarized by Austin (44) in the curves shown in

figure 10. Up to the A_2 point the form of this curve has been established and the accuracy of the best data is probably sufficient for

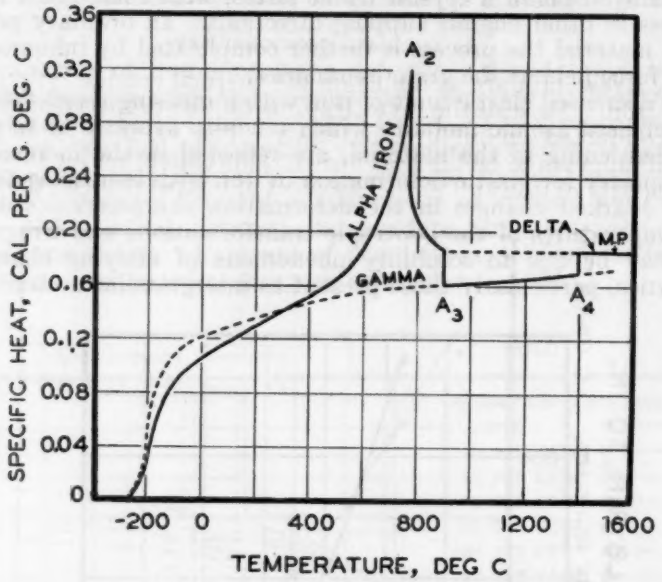

FIGURE 10.—*Specific heat of iron.*
[Austin (44).]

practical purposes. Above A_2, however, there is considerable uncertainty concerning the form of the curve as well as the numerical

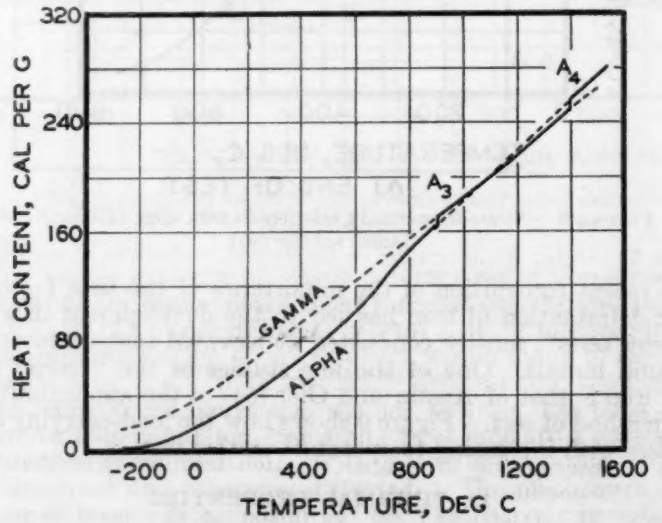

FIGURE 11.—*Heat content of iron.*
(Austin (45).]

values. There is need for more precise determinations of the heat capacity of gamma and delta iron.

Changes in the heat content at the transformation points, which are shown graphically in figure 11, amount to 3.86 cal/g at A_3 and 1.7 cal/g at A_4. There is apparently no heat effect at A_2.

(b) THERMAL CONDUCTIVITY

Only a few data are available on the thermal conductivity of high-purity iron. Most of the investigations on this property of iron have been conducted on impure materials. The value 0.19 cal/sec/cm² (°C/cm) appears to be the best present approximation for the thermal conductivity of iron at 0° C. The effect of temperature on the thermal

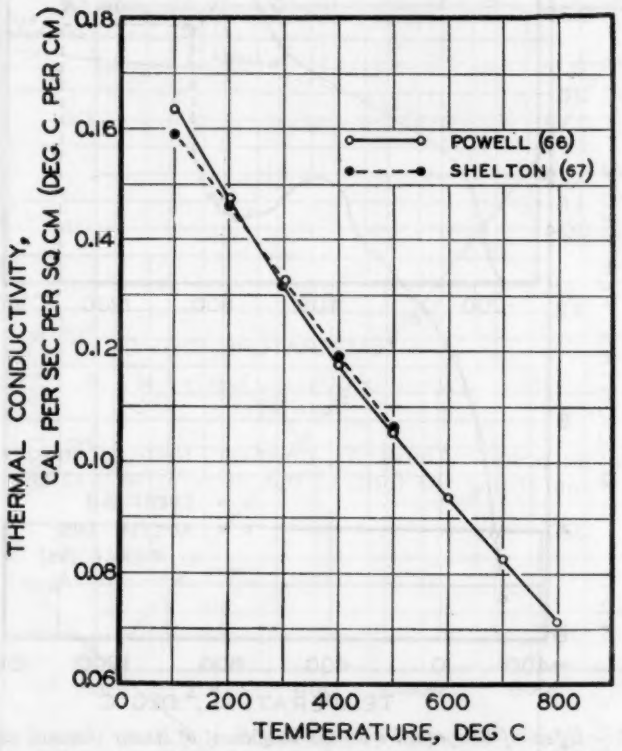

FIGURE 12.—*Effect of temperature on the thermal conductivity of open-hearth iron.*

conductivity of open-hearth (Armco) iron, according to the results of Powell (66) and Shelton (67), is shown in figure 12.

(c) THERMAL EXPANSIVITY

Much of the study of the thermal expansion of iron has been in connection with studies of allotropy, and the results are of greater value in determining the transformation temperatures than in determining the coefficient of thermal expansion.

Figure 13, illustrating the variation of the coefficient of linear thermal expansion of iron with temperature, is based mainly on the data of Ebert (31) and of Austin and Pierce (55). The precise determination of the coefficient becomes increasingly difficult with increasing temperature, and Austin and Pierce concluded that precise coefficients

cannot be given for the temperature range from 600° C to the A_3 point. The expansion may vary from sample to sample because of small differences in composition or previous treatment.

Solidification of molten iron is accompanied by a decrease in volume of about 5 percent. During the A_4 transformation there is a sudden contraction during cooling or an expansion during heating for which values ranging from 0.00085 to 0.0032 have been reported for $\Delta L/L$. The thermal expansion effect at A_3 is in the reverse direction to that at A_4; at A_3 there is a sudden contraction during heating and

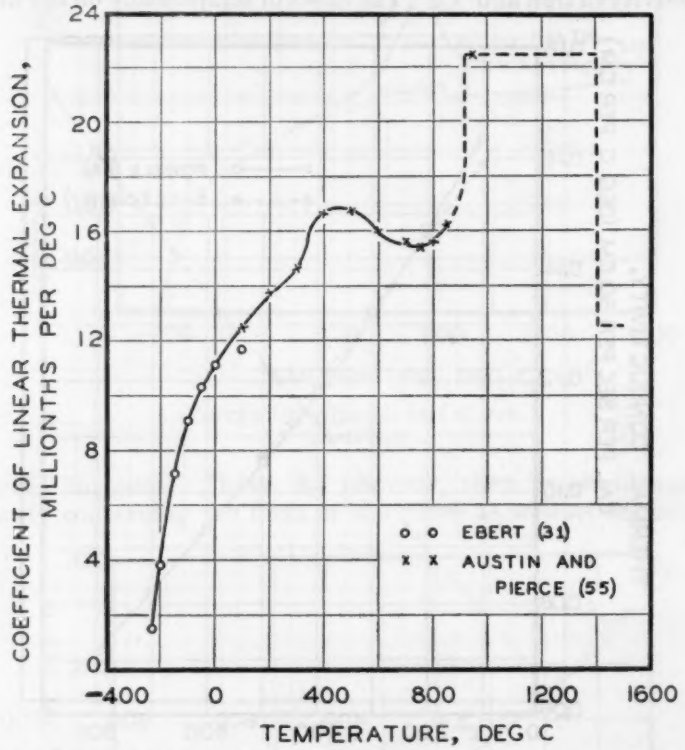

FIGURE 13.—*Effect of temperature on the coefficient of linear thermal expansion of iron.*

an expansion during cooling, with reported values for $\Delta L/L$ ranging from 0.00016 to 0.0038. The expansion and contraction of a particular sample are not always equal; permanent change in dimensions may result from repeated heating and cooling through A_3. Abnormality in thermal expansion has not been observed at A_2.

(d) THERMAL ELECTROMOTIVE FORCE

Although the thermal electromotive force of one pure metal against another is a constant for that particular combination, this property is considerably affected by the presence of local impurities and by the previous thermal and mechanical history of both metals. Sufficient data regarding the thermal electromotive force of pure iron and the effect of small amounts of impurities are not available as yet to permit the use of this determination as an indicator of purity in iron.

Thermocouples of iron with another metal such as aluminum, copper, lead, nickel, platinum, or tin have been studied but, in general, the thermal electromotive force of such a couple is small, varies in an irregular manner with temperature, and is not reproducible in other similar thermocouples. The only one which has been found useful is the combination of iron with constantan, the latter name being used to refer to a type of alloy rather than a single rigidly defined composition. Consequently, there are several constantans each with its own emf against iron. However, the relatively large potential developed by this combination and the approximately constant slope

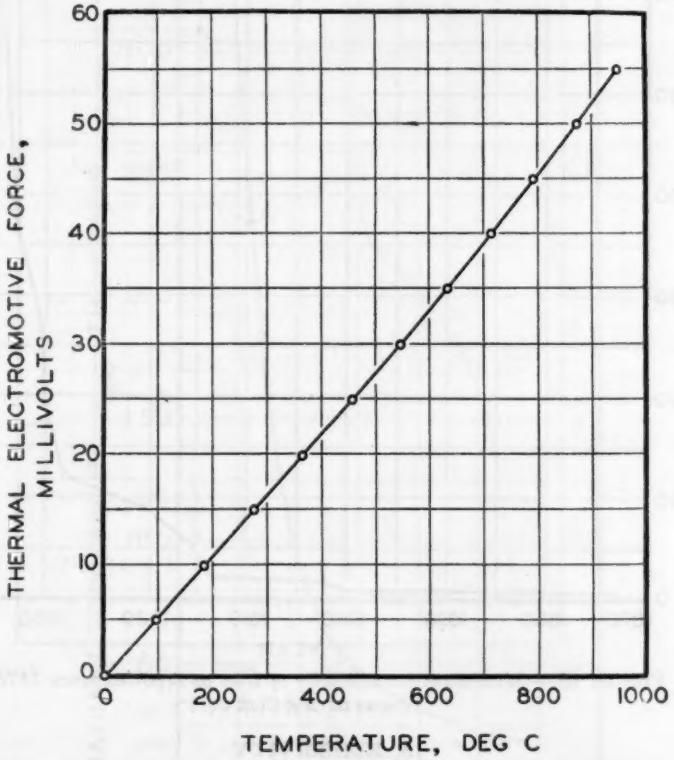

FIGURE 14.—*Thermal electromotive force of iron versus constantan.*
[International Critical Tables (25).]

of the curve between 0 and 1,000° C make it useful within this temperature range. Figure 14, showing the thermal electromotive force of an iron-constantan thermocouple at various temperatures, is typical of iron-constantan thermocouples in general, but the numerical values vary with different samples.

12. RESISTIVITY

The resistivity of iron is affected by the presence of impurities and by the previous mechanical and thermal treatment of the specimen. The effect of a given impurity is not always a linear one; for example, according to Yensen (19) a change in carbon content under 0.02

percent had eighteen times as much effect on the resistivity as did an equal change above 0.02 percent. Small changes in the resistivity as a result of application of pressure to the specimen have been reported by Beckman (7) and Bridgman (9).

A review of available information indicates that the rounded value, 9.8 microhm-cm, is the best approximation for the resistivity of iron at 20° C. Likewise, the rounded value 0.0065/° C appears to be the best approximation for the fundamental coefficient, i. e., the temperature coefficient of resistivity per degree between 0 and 100° C.

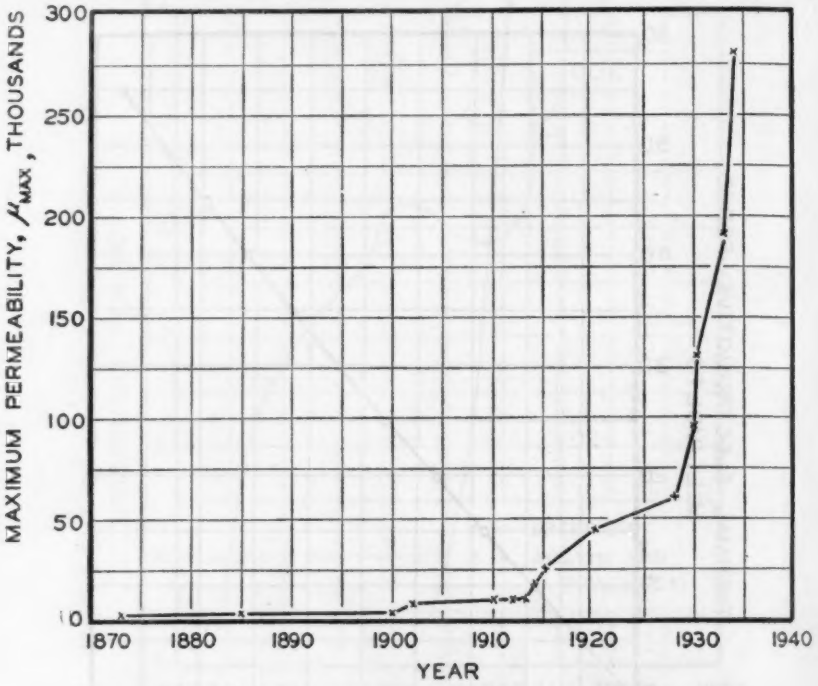

FIGURE 15.—*Maximum permeability of iron as reported since 1873.*
[Yensen (47) and Cioffi (58).]

13. EMISSIVITY

Emissivity is the ratio between the amounts of radiant energy emitted by iron and by a black body at the same temperature and is the only optical property of iron which is of practical importance. This property varies with the wave length of light and in optical pyrometry a correction is applied for the emissivity at an effective wave length of about 0.65 μ.

Few data are available on the emissivity of high-purity irons, but many determinations have been made on iron and steel under conditions of plant operation, on liquid steel containing slag and various floating objects, or on solid metal during hot-working operations when the surface was covered with a scale of iron oxide, for which values ranging from 40 to 90 percent have been reported. The emissivity for 0.65 μ of a bright surface of high-purity iron, either solid or liquid, according to the best available data (8) is about 37 percent.

14. MAGNETIC PROPERTIES

The magnetic properties of iron are so drastically affected by the presence of impurities, by the size and shape of the specimens, and by the previous thermal and mechanical treatment, that magnetic data, in general, represent the characteristics only of particular specimens. Appreciation of these factors has developed within quite recent years

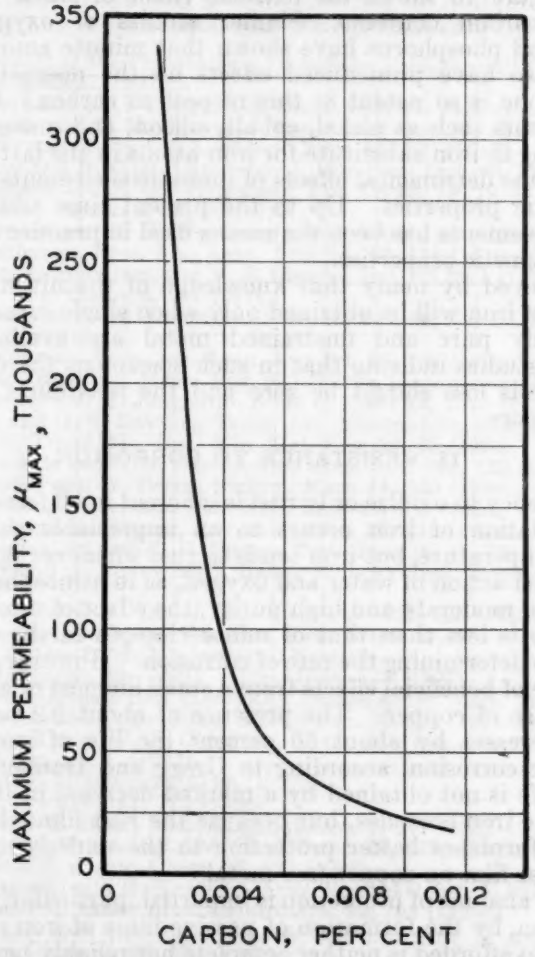

FIGURE 16.—*Effect of carbon content on the maximum permeability of a single crystal of oxygen-free iron.*

[Yensen and Ziegler (72).]

and is reflected in the changing opinion from year to year as to what constitutes the maximum in magnetic properties that can be obtained in iron. Figure 15 shows that relatively very low permeabilities were the best that could be obtained prior to 1900. The introduction of electrolytic iron about 1900 was accompanied by an improvement in magnetic properties which was negligible, however, in comparison with that which has been achieved since about 1914. The most recent

development is the treatment of high-purity iron in hydrogen at temperatures approaching the melting point, by which permeabilities as high as 280,000 have been attained.

Recent studies have shown that very small amounts of certain impurities, which because of their interstitial position distort the lattice structure, have surprisingly large effects on the magnetic properties of iron. The most striking effect so far reported is that of carbon; Figure 16 shows the extreme effect of small variations in very low carbon contents. Similar studies of oxygen, sulphur, nitrogen, and phosphorus have shown that minute amounts of these elements also have pronounced effects on the magnetic properties although none is so potent in this respect as carbon. On the other hand, elements such as nickel, cobalt, silicon, and manganese, which on dissolving in iron substitute for iron atoms in the lattice structure, counteract the detrimental effects of interstitial elements and improve the magnetic properties. Up to the present time addition of substitutional elements has been the means used in practice for obtaining superior magnetic properties.

It is believed by many that knowledge of the ultimate magnetic properties of iron will be obtained only when single-crystal specimens of absolutely pure and unstrained metal are available. Recent laboratory studies indicate that in such specimens the coercive force and hysteresis loss should be zero and the maximum permeability 500,000 or more.

15. RESISTANCE TO CORROSION

The tendency to oxidize or to rust is inherent in all ferrous materials. Direct oxidation of iron occurs to an appreciable extent only at elevated temperature, but iron tends to rust whenever it is exposed to the combined action of water and oxygen, as in atmospheric exposure.

In irons of moderate and high purity, the effect of minor changes in composition is less than that of minor changes in the conditions of exposure, in determining the rate of corrosion. However, an outstanding example of beneficial effects from a small amount of added element is in the case of copper. The presence of about 0.2 percent of this element increases by about 50 percent the life of iron exposed to atmospheric corrosion, according to Gregg and Daniloff (60). This increased life is not obtained by a marked decrease in the initial rate at which the iron corrodes, but because the rust film which forms on this metal furnishes better protection to the underlying metal than does the rust film on copper-free metal.

A certain amount of protection is imparted, particularly to the purer forms of iron, by the formation of passive films of iron oxide, but the protection so afforded is neither complete nor reliably permanent.

Satisfactory resistance to corrosion in ferrous metals is obtained only in the presence of substantial amounts of elements, for example silicon or chromium, the amount being such that the product should properly be considered an alloy.

16. MISCELLANEOUS PROPERTIES

There are a number of minor properties or effects which have received consideration by investigators. Included in this miscellaneous group are thermoelectric effects such as the Peltier and Thomson

effects, mechanomagnetic, galvanomagnetic, and thermomagnetic effects, reflectivity, and X-ray absorption. With one exception these properties or effects are of interest only in theoretical considerations. The one exception, which has a practical significance, is magnetostriction, the dimensional change during magnetization. This effect is believed to be largely responsible for the noise in electrical transformers and in loud speakers.

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RESEARCH PAPER RP861

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EFFECT OF YARN TWIST ON THE PROPERTIES OF CLOTH [1]

By Herbert F. Schiefer and Daniel H. Taft

ABSTRACT

The effect of warp and filling yarn twist on the breaking strength, elongation at rupture, and fabric assistance of cotton cloth is discussed for the plain and 2/2 basket weaves. In both weaves the number of warp and filling yarns per inch of cloth was kept constant at 34. The cloths were woven from 10s cotton yarn in various combinations of warp and filling twist multipliers, which varied from 2.5 to 9. The breaking strength and elongation at rupture of the cloths vary approximately with the breaking strength and elongation at rupture of the yarns from which the cloths were woven. The fabric assistance varies inversely with the breaking strength of the yarn. The direction of twist in the yarn has no significant effect on the results. The breaking strength, elongation at rupture, and fabric assistance are greater in the plain weave than in the 2/2 basket weave. The cloths were tested by the grab and strip methods, and the effect of the method of test is shown.

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I. INTRODUCTION

In order to design a cotton cloth having the optimum combination of properties for a given use, it is desirable if not essential to know how each of the properties in question is affected by the changes that can be made in the construction of the cloth. The study reported in this paper is one of several undertaken for the purpose of providing this information.[2]

This paper is concerned with the effect of varying the twist in the warp and the filling yarns on the breaking strength and elongation at rupture of plain-weave and 2/2 basket-weave cloths made from 10s (8.4 typp) cotton yarns. The results are correlated with the breaking strength and elongation of the yarns and with the type of test, whether strip or grab.

A somewhat similar study has been made by Essam,[3] who used 50s yarn spun from fine Sakellaridis cotton in 4 different twists. The

[1] The authors wish to acknowledge the assistance of A. A. Mercier, who initiated this investigation before he left the National Bureau of Standards.

[2] Herbert F. Schiefer, Richard S. Cleveland, John W. Porter, and Joshua Miller, *Effect of weave on the properties of cloth*, BS J. Research **11**, 441 (1933) RP600; Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns*, J. Research NBS **15**, 237 (1935) RP826; Herbert F. Schiefer, Daniel H. Taft, and John W. Porter, *Effect of number of warp and filling yarns per inch and some other elements of construction on the properties of cloth*, NBS J. Research **16**, 139 (1936) RP862.

[3] John M. Essam, *The physical properties of fabrics: The effect of yarn and weaving structure*, J. Textile Inst. **19**, T37 (1928); **20**, T275 (1929).

yarns of the 4 twists were each woven into cloths of 4 different weaves, using the same twist in the warp and filling yarns, and the same number of yarns per inch in the warp and filling.

II. PREPARATION OF CLOTHS

The cloths were woven from the 10s (8.4 typp) cotton yarn whose properties are described in Research Paper RP826. The cloths were woven in a plain weave and in a 2/2 basket weave. In both weaves the number of warp and filling yarns per inch was kept constant at 34. The cloths were approximately of the same weight, namely 5.1 oz/yd^2 for the basket weave, and 5.3 oz/yd^2 for the plain weave.

Five different twist multipliers were used in the warp yarn for the basket weave, and four different warp twist multipliers were used for the plain weave. Eight different twist multipliers were used in the filling yarn with each warp twist multiplier of the two weaves. Right-hand (Z) and left-hand (S) twists were used for each twist multiplier of the warp and filling yarns.

The relative humidity was maintained at approximately 65 percent during the weaving of these cloths.

Some of the cloths are shown in figures 1 and 2. They show the effect of the twist of the warp and filling yarns on the appearance of the cloths.

III. TEST PROCEDURE

The cloths were tested for breaking strength and elongation at rupture by the standard grab and strip methods.[4] Five determinations were made in the warp and in the filling direction of each cloth for each method of testing. The tests were made on a machine of the pendulum type having a capacity of 150 pounds. The specimens tested were in equilibrium with an atmosphere having a relative humidity of 65 percent and a temperature of 70° F.

IV. RESULTS

There appeared to be no consistent differences in the data for the cloths woven from yarns with right-hand and left-hand twists for each of the various combinations of warp and filling twist multipliers used. These results confirm those noted in Research Paper RP826 for cotton yarns. No distinction with respect to direction of twist is therefore made in the results presented.

The effect of changing the warp twist multiplier on the warp breaking strength and elongation at rupture of the cloths for each of the various filling twist multipliers is shown by the curves of figure 3. The curves at the bottom are for cloths in which the twist multiplier of the filling yarn is 2.5. Each value plotted is the average of 20 determinations, 5 made on each of 4 cloths. The remaining curves are for other cloths in which the indicated filling twist multipliers are used.

Similar results are given in figure 4 for the filling breaking strength and elongation at rupture of the cloths. The curves at the bottom show the variation with filling twist multiplier for cloths in which the twist multiplier of the warp yarn is 3. The remaining curves are for other cloths in which the indicated warp twist multipliers are used.

[4] Federal Specification for Textiles; Test Methods, CCC-T-191.

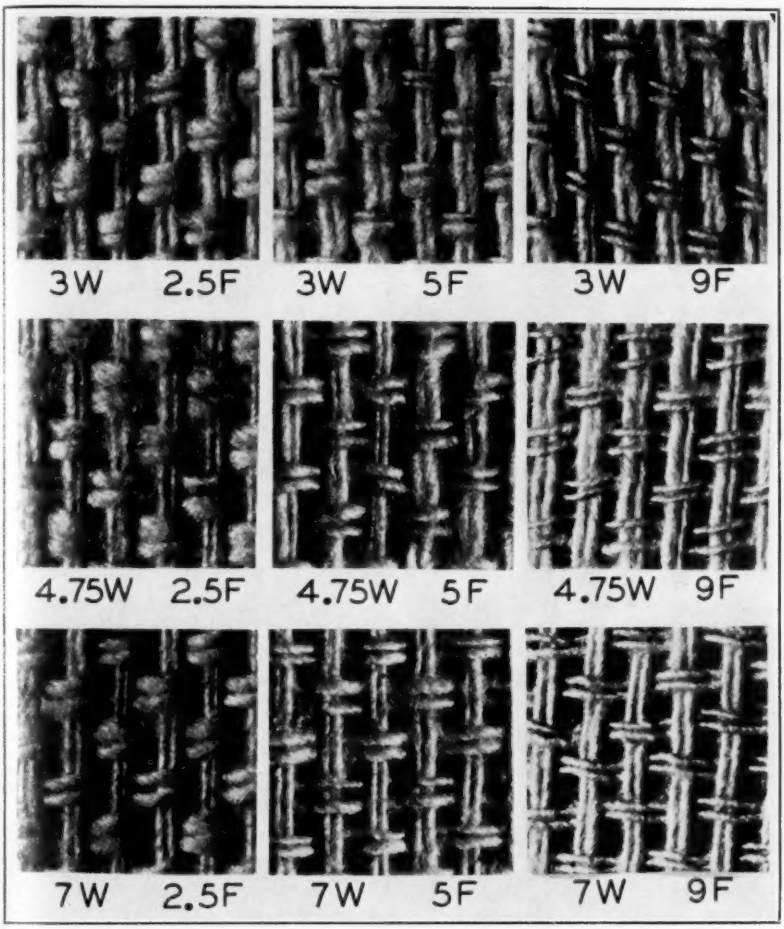

FIGURE 1.—*Effect of yarn twist on the appearance of 2/2 basket-weave cloth woven from 10s cotton yarn.*

The warp and filling twist multipliers are indicated by numbers. W and F refer to the warp (vertical) and filling (horizontal) yarns, respectively. Magnification about 4.

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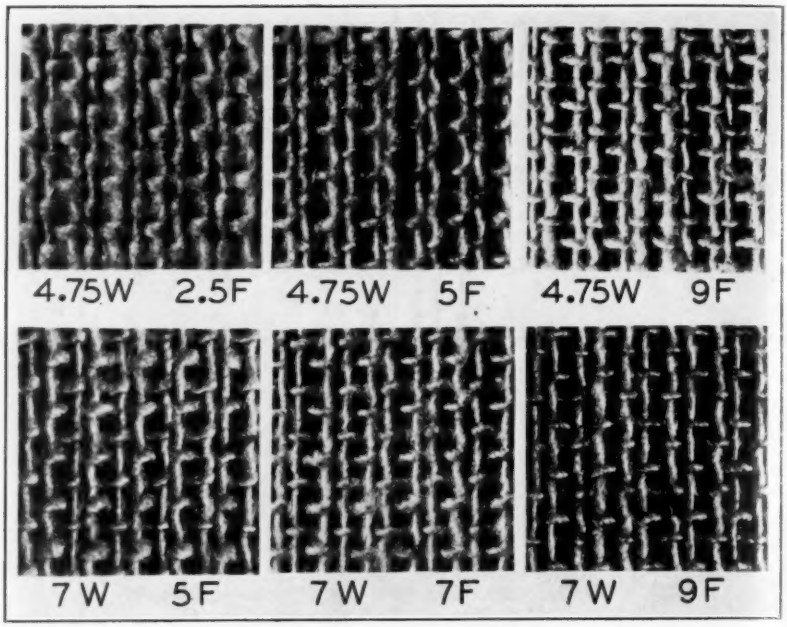

FIGURE 2.—*Effect of yarn twist on the appearance of plain-weave cloth woven from 10s cotton yarn.*

The warp and filling twist multipliers are indicated by numbers. W and F refer to the warp (vertical) and filling (horizontal) yarns, respectively. Magnification about 4.

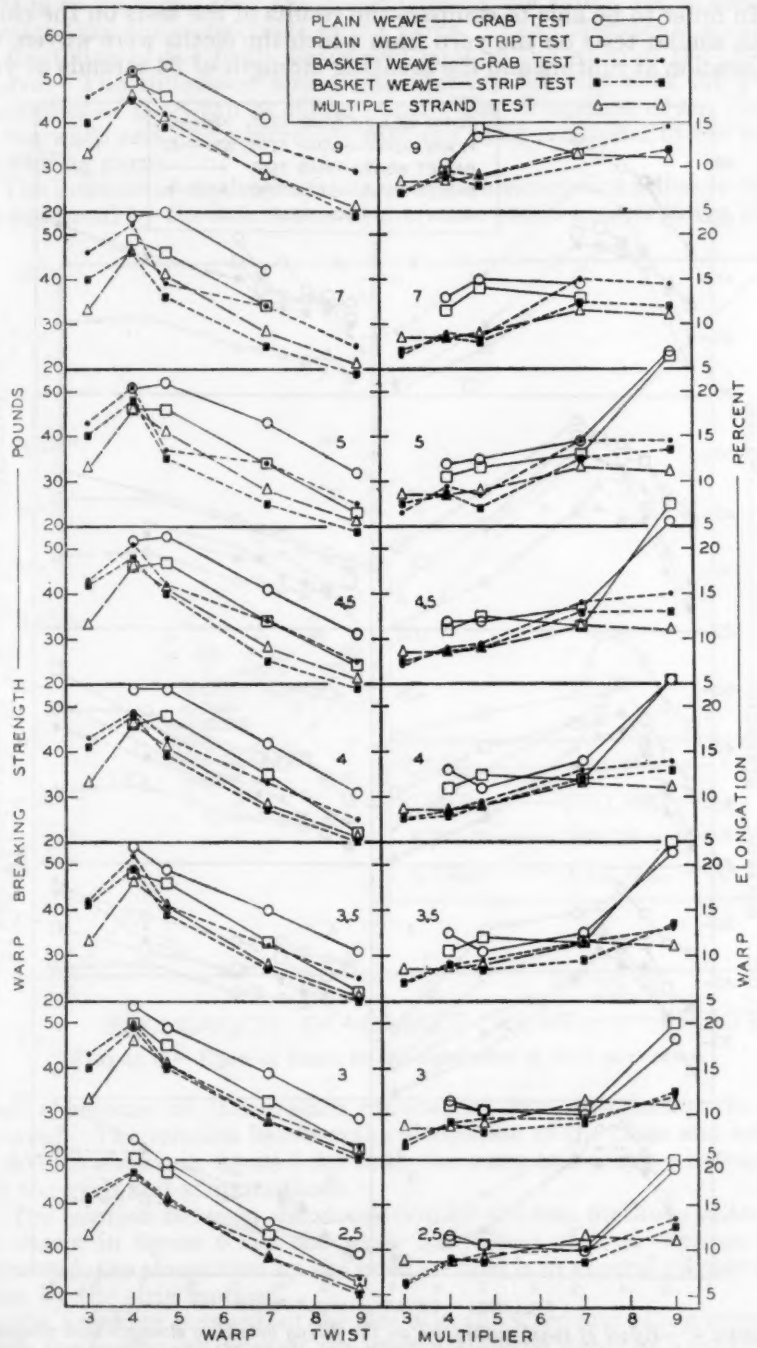

FIGURE 3.—*Effect of twist multiplier on the warp breaking strength and elongation at rupture of cloth woven from 10s cotton yarn.*

The number associated with each group of curves represents the filling twist multiplier.

In order to be able to compare the results of the tests on the cloths with similar tests on the yarn from which the cloths were woven, the elongation at rupture and the breaking strength of 34 strands of yarn

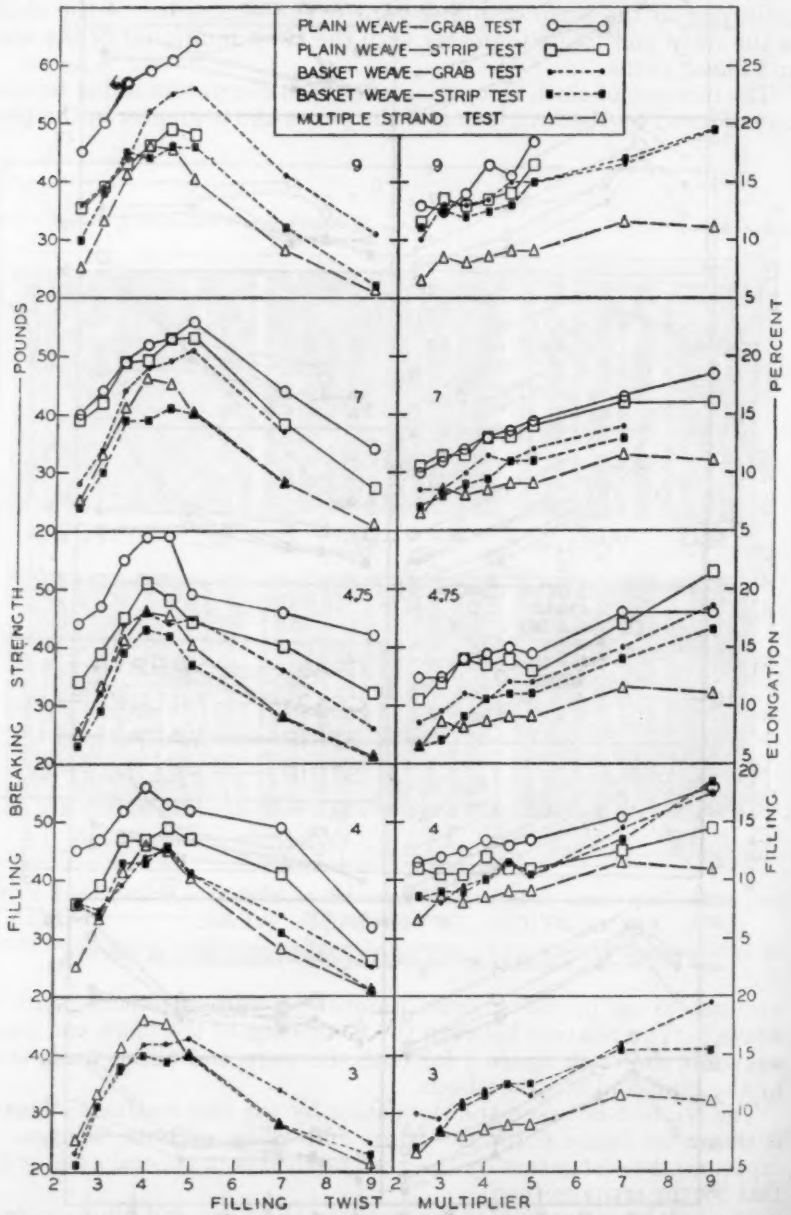

FIGURE 4.—*Effect of twist multiplier on the filling breaking strength and elongation at rupture of cloth woven from 10s cotton yarn.*

The number associated with each group of curves represents the warp twist multiplier.

on the basis of the multiple-strand test are also plotted in figures 3 and 4.

It is to be noted that the elongations of the cloths are in general greater than the elongations of the yarns. The difference is greatest in the filling of the plain weave and least in the warp of the basket weave. The difference appears to increase slightly with the twist multiplier of the warp or filling yarn. The elongation of the cloths in the warp and filling increases with the twist multiplier of the warp and filling yarns.

The increase of cloth elongation over yarn elongation is due to take-up produced by the interlacing of the yarns and is greater in the plain

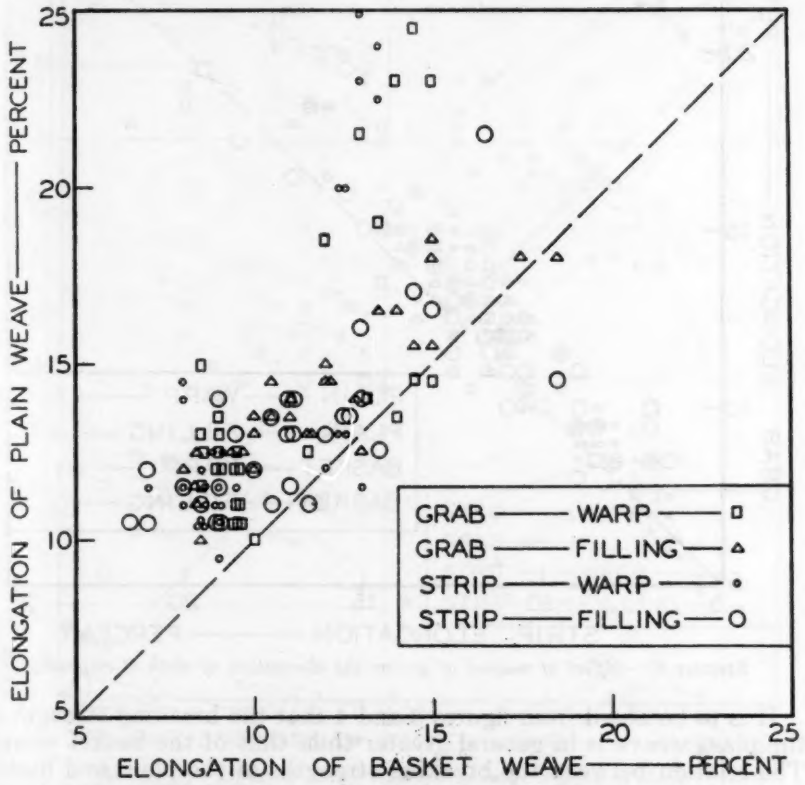

FIGURE 5.—*Effect of weave on the elongation of cloth at rupture.*

weave because of the greater number of yarn interlacings in this weave.[5] The relation between the elongation of the plain and basket weaves is shown in figure 5 for both the warp and filling when tested by the grab and strip methods.

The relation between the elongation by the two methods of testing is shown in figure 6 for the warp and filling of both weaves. As expected, the elongation by the grab method is in general greater than that by the strip method.

The breaking strength of the cloths in the warp and filling increases with the twist multiplier of the warp and filling yarns to a maximum

[5] Herbert F. Schiefer, Richard S. Cleveland, John W. Porter, and Joshua Miller, *Effect of weave on the properties of cloth.* BS J. Research 11, 441 (1934) RP600.

and then decreases for high twist multipliers in the same manner in which the breaking strengths of the yarns vary with twist multiplier.[6] In general these cloths reach a maximum breaking strength in either the warp or filling at a twist multiplier between 4 and 4.75.

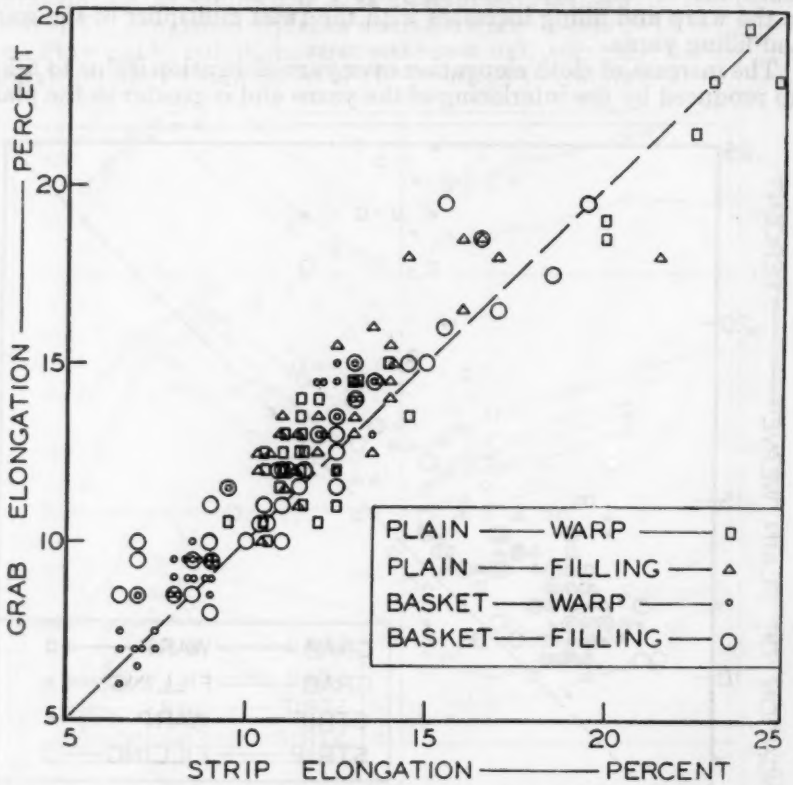

FIGURE 6.—*Effect of method of test on the elongation of cloth at rupture.*

It is to be noted from figures 3 and 4 that the breaking strength of the plain weave is in general greater than that of the basket weave. The relation between the breaking strengths of the plain and basket weaves is shown in figure 7 for both the warp and filling when tested by the grab and strip methods.

The relation between the breaking strength by the two methods of testing is shown in figure 8 for the warp and filling of both weaves.

[6] Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns.* J. Research, NBS 15, 237 (1935) RP826.

As expected, the breaking strength by the grab method is in general greater than that by the strip method.

The difference between the breaking strength of the cloth and the breaking strength of 34 strands of yarn on the basis of the multiple strand test of the yarn, expressed as a percentage of the breaking strength of 34 strands of yarn is known as fabric assistance. The relation between fabric assistance and the twist multiplier of the warp and filling yarns is shown in figure 9. It is to be noted that the fabric

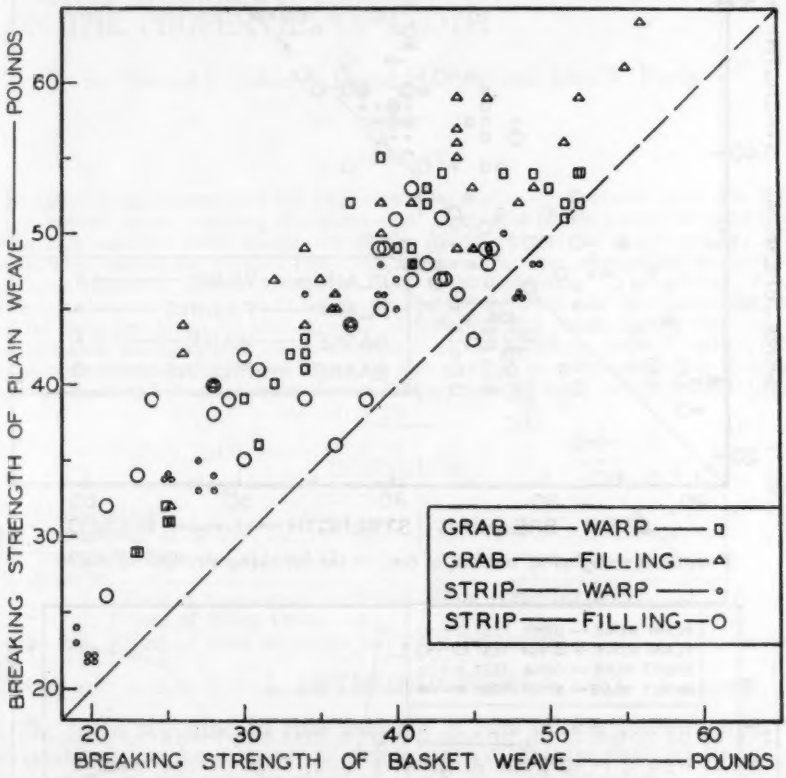

FIGURE 7.—*Effect of weave on the breaking strength of cloth.*

assistance decreases in general with an increase in twist multiplier to a minimum and then increases for high twist multipliers. Minimum fabric assistance is obtained at the twist multiplier which yields, in general, a maximum strength in the yarn and also in the cloth. The fabric assistance is greater in the plain weave than in the basket weave. This difference may be attributed to the greater number of yarn interlacings in the plain weave.[7] The effect of the method of

[7] See footnote 5.

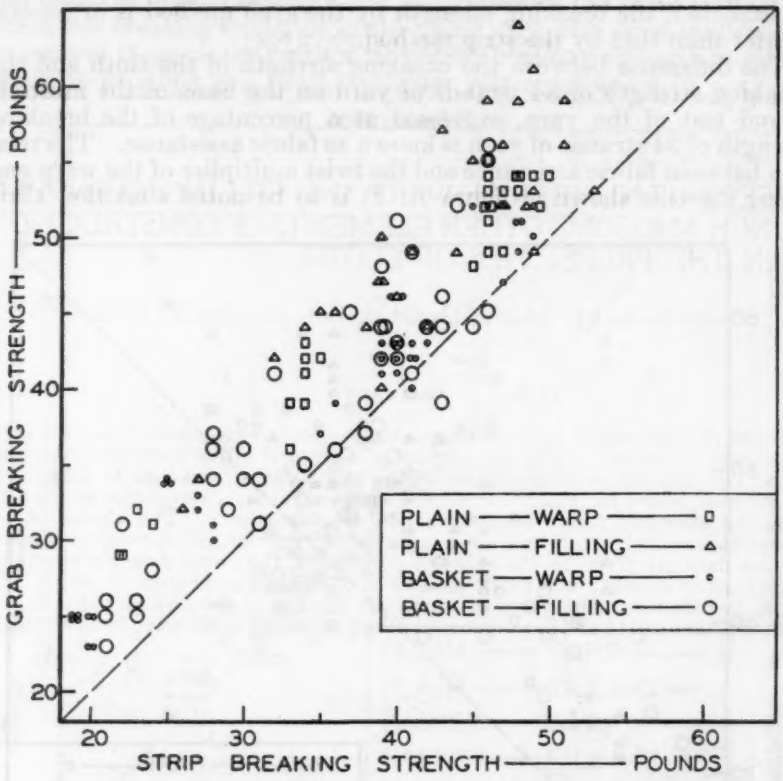

FIGURE 8.—*Effect of method of test on the breaking strength of cloth.*

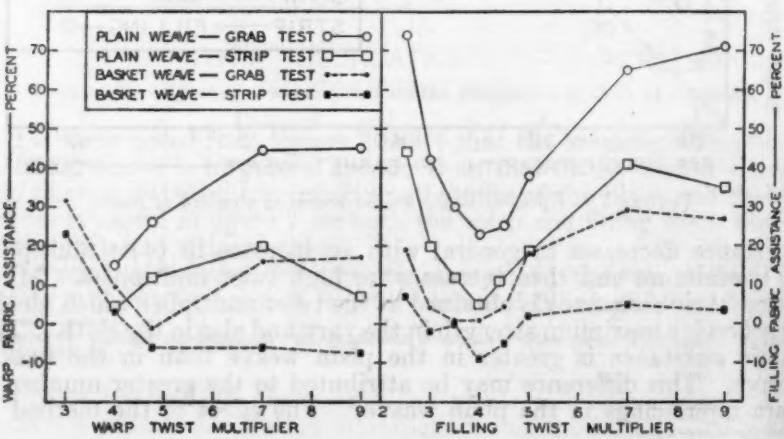
PLAIN WEAVE — GRAB TEST
PLAIN WEAVE — STRIP TEST
BASKET WEAVE — GRAB TEST
BASKET WEAVE — STRIP TEST
WARP FABRIC ASSISTANCE — PERCENT
FILLING FABRIC ASSISTANCE — PERCENT
WARP TWIST MULTIPLIER
FILLING TWIST MULTIPLIER

FIGURE 9.—*Effect of twist multiplier on fabric assistance.*

testing on the fabric assistance is also indicated by the curves of figure 9.

WASHINGTON, December 30, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP862

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EFFECT OF NUMBER OF WARP AND FILLING YARNS PER INCH AND SOME OTHER ELEMENTS OF CONSTRUCTION ON THE PROPERTIES OF CLOTH

By Herbert F. Schiefer, Daniel H. Taft, and John W. Porter

ABSTRACT

Series of plain-weave and 3/3 basket-weave cloths were woven from 80s (67.2 typp) cotton yarns, varying the number of warp and filling yarns per inch from 80 to 120, and the twist multiplier of the filling yarns from 2.48 to 5.64. The cloths were tested for weight, thickness, air permeability, elongation at rupture, breaking strength, fabric assistance, and tear resistance. The effects of the variations in construction on these properties are reported and discussed. Experimental data are given on the effect of abrasion of the yarns during weaving on the breaking strength and fabric assistance of cloths woven from 2/140 (2/117.6 typp) mercerized-cotton yarns in which the number of warp yarns per inch was kept constant at 114 and the number of filling yarns per inch varied from 30 to120.

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I. INTRODUCTION

The work reported in this paper is a part of the general program undertaken for the purpose of providing systematic data on the effect of changes in the construction of cloth on its properties.[1] It is concerned with the effect of changes in the number of warp and filling yarns per inch on the weight, thickness, air permeability, elongation at rupture, breaking strength, fabric assistance, and tear resistance of plain weave and 3/3 basket-weave cloths woven from 80s (67.2 typp) cotton yarns. The effect of changes in the twist of the filling yarns, which supplements the study reported in Research Paper RP 861, also received consideration.

A somewhat similar study has been made by Essam [2] who used 50s yarn, spun from fine Sakellaridis cotton, for cloths woven in

[1] Other papers include the following: Herbert F. Schiefer, Richard S. Cleveland, John W. Porter, and Joshua Miller, *Effect of weave on the properties of cloth*, BS J. Research **11**, 441 (1933) RP600; Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns*, J. Research NBS **15**, 237 (1935) RP826; Herbert F. Schiefer and Daniel H. Taft, *Effect of yarn twist on the properties of cloth*, J. Research NBS **16**, 131 (1936), RP861.

[2] John M. Essam, *The physical properties of fabrics: The effect of yarn and weaving structure*, J. Textile Inst. **19**, T37 (1928); **20**, T275 (1929).

4 different weaves. The cloths of the 4 weaves were each woven with 4 different numbers of yarns per inch, using the same number of yarns per inch in the warp and filling.

The strength of a cloth can be correlated with that of the yarns from which it is made only by taking account of the effect on the yarn of abrasion during weaving, and of the fabric assistance, i. e., the contribution of the warp yarns to the filling breaking strength, and of the filling yarns to the warp breaking strength of the cloths. These effects were studied on some cloths woven from 2/140 (2/117.6 typp) mercerized cotton yarns and are discussed in this paper.

II. PREPARATION OF CLOTHS

A series of cloths was woven from 80s (67.2 typp) cotton yarns whose properties are described in a previous paper.[3] The cloths were woven in the plain and the 3/3 basket weaves. In both weaves the number of warp yarns per inch of cloth was 80, 100, and 120, respectively. For each of the three warp constructions the number of filling yarns per inch of cloth was 80, 90, 100, 110, and 120, respectively. The twist multiplier of the warp yarn in these cloths was 3.33, and the twist multiplier of the filling yarn was 2.93.

A second series of cloths was woven from the same 80s yarns with 100 yarns per inch of cloth in the warp and with 96 in the filling. The twist multiplier of the warp yarn was 3.33, as before. This series varied with respect to the twist multipliers of the filling yarns, which were 2.48, 2.93, 3.33, 4.07, and 5.64.

A third series of plain-weave cloths was woven in which the warp and filling yarns were 2/140 (2/117.6 typp) mercerized cotton. The cloths were woven with 114 yarns per inch of cloth in the warp, and with 30, 40, 50, 60, 70, 80, 90, 100, and 120 yarns per inch, respectively, in the filling. In connection with the weaving of each cloth, the loom was operated to weave a length of 3 inches with an empty shuttle to provide material for the determination of the effect of loom abrasion on the breaking strength of the warp yarns, and also the effect of interlacing the warp yarns with filling yarns on the warp breaking strength and fabric assistance. In another portion of the cloths the warp yarns were cut out for a width of 3 inches to provide material for the determination of the effect of interlacing the filling yarns with warp yarns on the filling breaking strength and fabric assistance.

The relative humidity of the atmosphere was maintained at approximately 65 percent during the weaving of the cloths.

The effect of changes in construction on the appearance of the cloths is shown in the photographs reproduced in figures 1 and 2.

III. TEST PROCEDURE

Atmospheric humidity.—All tests were made on material in equilibrium with an atmosphere having a relative humidity of 65 percent and a temperature of 70° F.

Weight.—Five specimens, each 2 inches square, were cut with a die from each cloth and weighed on an analytical balance. The weight of the 5 specimens, expressed in ounces per square yard, is reported in this paper for each cloth.

[3] Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns*, J. Research NBS 15, 237 (1935) RP826.

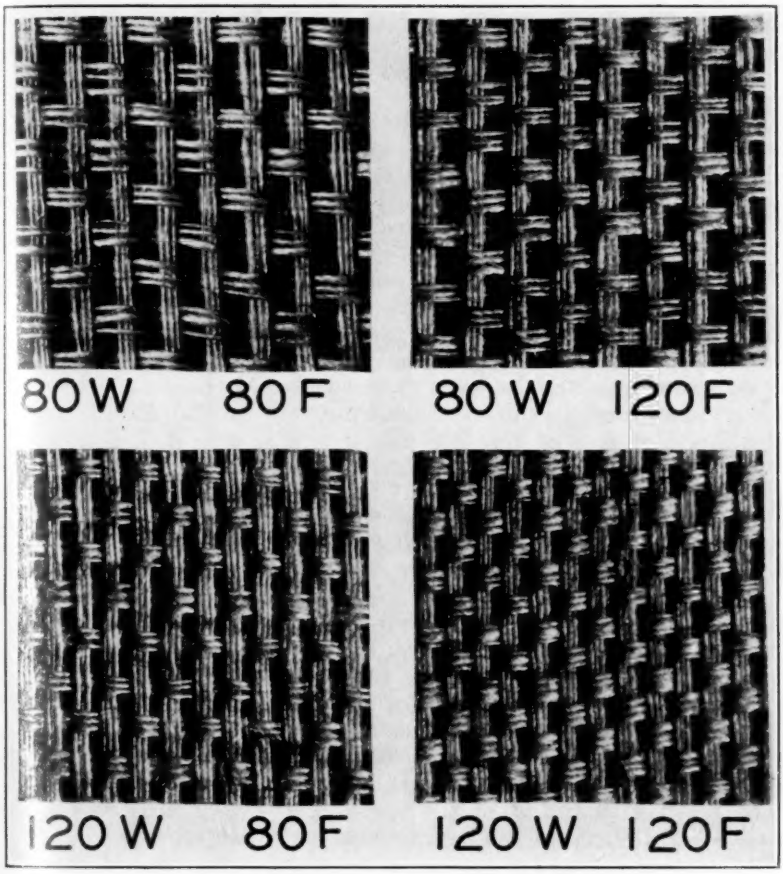

FIGURE 1.—*Effect of number of warp and filling yarns per inch on the appearance of 3/3 basket-weave cloth woven from 80s cotton yarn.*

The number of yarns per inch are indicated. W and F refer to the warp (vertical) and filling (horizontal) yarns, respectively. Magnification about 6.5.

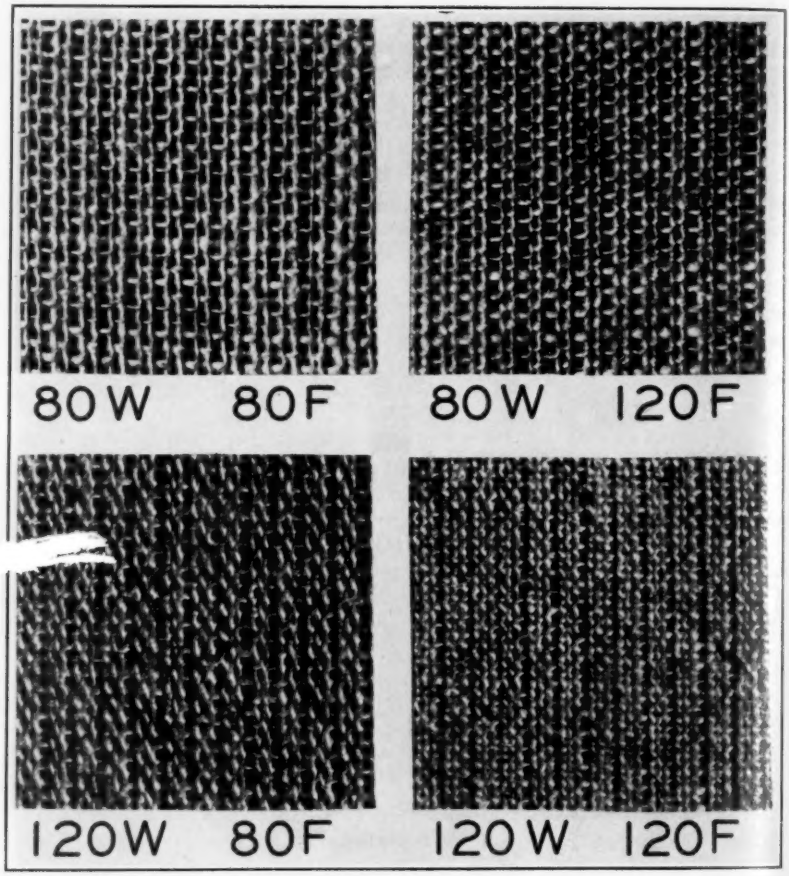

FIGURE 2.—*Effect of number of warp and filling yarns per inch on the appearance of plain-weave cloth woven from 80s cotton yarn.*

The number of yarns per inch are indicated. W and F refer to the warp (vertical) and filling (horizontal) yarns, respectively. Magnification about 6.5.

Thickness.—The thickness of each cloth was measured at 10 areas with the compressometer,[4] using a circular foot 1 inch in diameter and exerting a pressure of 1 lb/in^2. The average of the 10 determinations on each cloth is reported to the nearest 0.0005 inch.

Air permeability.—Three air-permeability determinations were made on each cloth according to the method described by Schiefer and Best.[5] The average result of the 3 tests on each cloth, expressed in cubic feet per minute per square foot of cloth at a pressure drop of 0.5 inch of water across the cloth, is reported in this paper.

Breaking strength and elongation at rupture.—The cloths were tested for breaking strength and elongation at rupture by the standard strip method.[6] Five determinations were made in the warp and five in the filling direction of each cloth. The tests were made on a machine of the pendulum type having a capacity of 55 pounds.

In the third series of cloths, strips 1 inch in width and about 12 inches in length were taken from the warp and filling in such a manner that the strips included the portions in which the warp (or filling) yarns were not interlaced with filling (or warp) yarns. One-half of each strip was tested for breaking strength of the cloth while the other half was tested for the breaking strength of the yarns which had been subjected to the actions of the loom. The breaking strengths of the warp and filling yarns were also determined by the multiple-strand method.[7]

Fabric assistance is computed from the difference in breaking strength of the cloth and the breaking strength of the yarns tested by the multiple-strand method. In the third series of cloths fabric assistance is also computed from the difference in breaking strength of the cloths and the breaking strength of the yarns which had been subjected to the actions of the loom.

Tear resistance.—The tear resistance was determined from specimens 3 inches wide and 6 inches long, according to the preferred method of the American Society for Testing Materials.[8] The average result of 5 tests in the warp direction and of 5 tests in the filling direction is reported for each cloth.

IV. RESULTS

1. EFFECT OF NUMBER OF WARP AND FILLING YARNS PER INCH

The effect of varying the number of warp and filling yarns per inch of cloth on the weight, thickness, air permeability, elongation at rupture, breaking strength, fabric assistance, and tear resistance of the basket- and plain-weave cloths is shown by the data given in table 1.

With only a few exceptions, the weight of the cloth is directly proportional to the sum of the number of warp and filling yarns per inch. There is no marked difference in the weight between similar cloths of the 2 weaves.

[4] Herbert F. Schiefer, *The compressometer, an instrument for evaluating the thickness, compressibility, and compressional resilience of textiles and similar materials*, BS J. Research **10**, 705 (1933) RP561.
[5] *A portable instrument for measuring air permeability of fabrics*, BS J. Research **6**, 51 (1931) RP261.
[6] Federal Specification for Textiles; Test Methods, CCC-T-191.
[7] C. W. Schoffstall and H. A. Hamm, *A multiple-strand test for yarns*, BS J. Research **2**, 871 (1929) RP61
[8] ASTM Standards on Textile Materials, ASTM designation D39-34, p. 8 (October 1935).

TABLE 1.—*Effect of number of warp and filling yarns per inch of cloth on the properties of cloth woven from 80s cotton yarn*

Warp yarns per inch	3/3 BASKET WEAVE					PLAIN WEAVE				
	Filling yarns per inch									
	80	90	100	110	120	80	90	100	110	120
Weight Per Square Yard, Ounces										
80	1.6	1.7	1.8	1.9	2.0	1.5	1.7	1.8	1.9	2.0
100	1.8	1.9	2.0	2.1	2.2	1.7	1.9	2.0	2.1	2.2
120	1.9	2.0	2.1	2.2	2.3	2.0	2.1	2.2	2.3	2.4
Thickness, Inch										
80	0.010	0.011	0.0115	0.0115	0.012	0.0075	0.008	0.008	0.008	0.008
100	.0095	.010	.0105	.011	.0115	.009	.0085	.0085	.0085	.0085
120	.010	.010	.0105	.0105	.011	.009	.009	.009	.009	.009
Air Permeability [1]										
80	663	579	515	439	402	416	317	254	195	175
100	441	390	318	307	264	295	243	195	167	124
120	394	354	297	259	221	290	211	162	125	99
Filling Elongation, Percent										
80	9	11	13	13	13	11	13	14	16	19
100	11	11	12	13	14	14	15	16	17	18
120	10	12	13	14	16	14	14	16	16	18
Warp Elongation, Percent										
80	10	10	10	10	10	12	12	11	12	13
100	12	11	12	12	12	16	17	18	18	20
120	14	14	14	15	14	21	19	21	20	23
Filling Breaking Strength, Pounds										
80	17	20	23	27	29	21	25	29	34	38
100	21	22	25	29	31	24	28	31	33	39
120	20	24	25	28	33	26	29	33	34	36
Warp Breaking Strength, Pounds										
80	23	23	23	23	23	25	24	24	25	25
100	29	29	29	29	28	31	32	30	29	27
120	36	35	35	36	35	35	34	31	33	29
Filling Fabric Assistance, Percent										
80	−6	−1	5	9	9	17	23	32	39	41
100	12	8	10	17	15	34	40	40	34	45
120	11	19	14	15	23	45	40	50	39	34
Warp Fabric Assistance, Percent										
80	23	21	21	21	20	32	26	26	32	32
100	22	22	22	22	18	28	32	24	20	12
120	26	23	23	26	23	25	21	12	17	3

[1] Cubic feet per minute per square foot of cloth at a pressure drop of 0.5 inch of water across the cloth.

TABLE 1.—*Effect of number of warp and filling yarns per inch of cloth on the properties of cloth woven from 80s cotton yarn*—Continued

Warp yarns per inch	3/3 BASKET WEAVE					PLAIN WEAVE				
	Filling yarns per inch									
	80	90	100	110	120	80	90	100	110	120
	Filling Tear Resistance, Pounds									
80	4	5	4	5	5	3	3	3	3	3
100	4	4	5	5	6	2	3	3	3	3
120	4	4	4	5	4	2	2	3	2	2
	Warp Tear Resistance, Pounds									
80	5	4	4	4	4	3	4	4	3	3
100	5	6	6	5	5	5	3	3	3	3
120	6	7	7	6	6	3	4	3	4	3

The number and warp of filling yarns per inch does not affect the thickness of the cloths appreciably, although there is a slight tendency for the cloths to increase in thickness with the increase in the number of filling yarns. The difference in thickness between corresponding cloths of the basket and plain weaves is marked. The cloths of the basket weave, which have a fewer number of yarn interlacings, are thicker than corresponding cloths of the plain weave. The yarns of these cloths are of fairly low twist, that is, yarns of relatively large diameter which may be easily compressed. The difference in thickness between corresponding cloths of the two weaves may be attributed to the greater compression of the yarns in the plain weave resulting from the greater number of yarn interlacings.

The air permeability decreases greatly with an increase in the number of yarns per inch in either the warp or filling direction of the cloth. As expected, the air permeability of cloths of the basket weave is considerably greater than that of corresponding cloths of the plain weave. An increase of 50 percent in the sum of the number of warp and filling yarns per inch increases the weight by about 50 percent and decreases the air permeability to about one-fourth in the plain weave and to about one-third in the basket weave.

The elongation at rupture increases with the number of warp and filling yarns per inch. This increase is attributable to the increase in take-up resulting from the increase in the number of yarn interlacings. The elongation of cloths of the plain weave is greater than that of corresponding cloths of the basket weave for the same reason, which is in agreement with the results reported in Research Papers RP600 and RP861 and by Essam.

The filling and warp breaking strengths increase with the number of filling and warp yarns per inch, respectively. The breaking strengths are also affected by such factors as yarn twist, number of yarn interlacings, and loom abrasion. The effect of these factors is brought out clearly by the values for fabric assistance, in which the breaking strength of the yarn and the number of yarns per inch are taken into consideration.

The filling fabric assistance increases slightly with the increase in the number of warp yarns per inch and also with the increase in the number of filling yarns per inch. This increase is quite appreciable in the basket-weave cloths and in the plain-weave cloths which have a low number of filling or warp yarns per inch. It is attributable to the increase in the breaking strength of the cloths resulting from the increase in the number of yarn interlacings. It should be noted, however, that the filling fabric assistance of the plain weave decreases for cloths having a high number of filling or warp yarns per inch. For these cloths the yarns are packed very tightly resulting in great strains on the filling yarns. The number of yarn interlacings in these cloths exceeds the number usually considered satisfactory for good weaving.

The warp fabric assistance increases slightly with the increase in the number of warp yarns per inch for the basket weave. This increase is attributable to the increase in the number of yarn interlacings. The warp fabric assistance decreases slightly with the increase in the number of filling yarns per inch in both weaves. An increase should result because of the increase in the number of yarn interlacings. The decrease is attributable to abrasion of the warp yarns by the loom, which increases directly with the number of filling yarns per inch.

The warp fabric assistance decreases markedly in the plain weave with the increase in the number of warp or filling yarns per inch. The loom abrasion is more severe in the plain weave than in the 3/3 basket weave. This increase in loom abrasion and the great packing of the warp and filling yarns in the plain weave account for its low fabric assistance in the warp direction.

The fabric assistance is in general greater in the plain weave than in corresponding cloths of the basket weave, which is in agreement with the results reported in Research Papers RP600 and RP861 and by Essam. An exception should be noted, however, in the warp fabric assistance for the cloths having a high number of warp and filling yarns per inch for which the warp fabric assistance of the basket weave exceeds that of the plain weave. This effect is attributable to the larger number of yarn interlacings and to the greater packing of warp and filling yarns in the plain weave, resulting in greater loom abrasion and poor weaving.

The tear resistance depends upon the freedom of movement of the warp and filling yarns and upon the elongation and breaking strength of the yarns. The number of warp and filling yarns appear to have little effect on the tear resistance. The tear resistance is greater for the basket weave, which is more open and contains fewer yarn interlacings than the plain weave, which is in agreement with the results noted in Research Paper RP600. The tear resistance of the warp is greater than that of the filling. This difference is attributable to the fact that the elongation and breaking strength are greater for the warp yarns than for the filling yarns.

2. EFFECT OF FILLING TWIST

The effect of changing the twist multiplier of the filling yarn on the properties of 3/3 basket-weave and plain-weave cloths is shown by the data given in table 2.

TABLE 2.—*Effect of filling twist on the properties of cloth woven from 80s cotton yarn in which the twist multiplier of the warp yarn is 3.33, with 100 yarns per inch in the warp and with 96 yarns per inch in the filling*

Designation		3/3 Basket weave					Plain weave				
Filling twist multiplier		2.48	2.93	3.33	4.07	5.64	2.48	2.93	3.33	4.07	5.64
Weight, oz/yd²		2	2	2	2	2	2	2	2	2	2
Thickness, in.		0.010	0.010	0.011	0.011	0.0115	0.0085	0.008	0.008	0.008	0.0085
Air permeability [1]		357	383	430	497	547	169	203	222	252	290
Elongation, %	W	11	12	12	12	12	17	16	17	17	19
	F	11	12	13	13	15	15	16	15	15	19
Breaking strength, lb	W	29	31	30	29	30	31	31	32	31	31
	F	20	24	27	25	21	31	31	32	30	31
Fabric assistance, %	W	20	25	20	16	20	26	26	30	26	26
	F	−1	11	18	14	19	56	44	40	35	73
Tear resistance, lb	W	5	6	5	5	5	3	3	3	3	2
	F	4	4	5	5	6	2	3	3	3	3

[1] Cubic feet per minute per square foot of cloth at a pressure drop of 0.5 inch of water across the cloth.

The weight of the cloths is not affected by a change in the filling twist, which is in agreement with the results noted in Research Paper RP861 for cloths woven from 10s cotton yarns.

The thickness of the basket-weave cloths increases slightly with the increase in the twist of the filling yarns. The thickness of the plain-weave cloth is not affected by the filling twist. The thickness of the plain-weave cloths is considerably less than that of the basket-weave cloths, a fact already noted earlier in this paper.

The air permeability increases greatly with the increase in the filling twist. It is considerably lower for the plain-weave cloths than for corresponding cloths of the basket weave.

The warp elongation at rupture varies little with the increase in twist of the filling yarns. The increase in the filling elongation of the cloths is attributable to the increase in elongation of the yarns resulting from higher twist. The difference in elongation between corresponding cloths of the plain and basket weaves is attributable to the difference in take-up resulting from the number of yarn interlacings.

The warp breaking strength and fabric assistance are affected very little by the twist of the filling yarns. The filling breaking strength, however, increases to a maximum at the filling twist multiplier 3.33, the twist multiplier at which the breaking strength of the yarn is a maximum,[9] and then decreases for higher twists. The variation is greater in the basket weave. The breaking strength and fabric assistance are greater in the plain weave. The variations in the results for elongation, breaking strength, and fabric assistance of this series of cloths with the increase in the filling twist are in substantial agreement with those noted in Research Paper RP861 for cloths woven from 10s cotton yarns.

The filling tear resistance appears to increase slightly with the twist of the filling yarns. This increase is attributable to the increase in elongation and to the increase in the freedom of movement of the filling yarns of higher twist because of their smaller diameter and smoother surface. The tear resistance of the basket-weave cloths is greater than that of the plain weave, because of the greater freedom of movement of the yarns in the direction of the tear.

[9] Herbert F. Schiefer and Daniel H. Taft, *Mechanical properties of cotton yarns*, J. Research NBS 15, 237 (1935), RP826.

3. EFFECT OF LOOM ABRASION AND YARN INTERLACING

The effect of loom abrasion and of yarn interlacing on the breaking strength and fabric assistance of cloths, in which the number of warp yarns per inch was kept constant at 114 and the number of filling yarns per inch was varied, is shown by the curves in figure 3. The lower group of curves gives the warp and filling breaking strength of the cloths, the breaking strength of the warp and filling yarns which had been subjected to the actions of the loom, and the breaking strength of the warp and filling yarns tested by the multiple-strand method. The upper group of curves gives the warp and filling fabric assistance of the cloths based upon the breaking strength of the yarns which

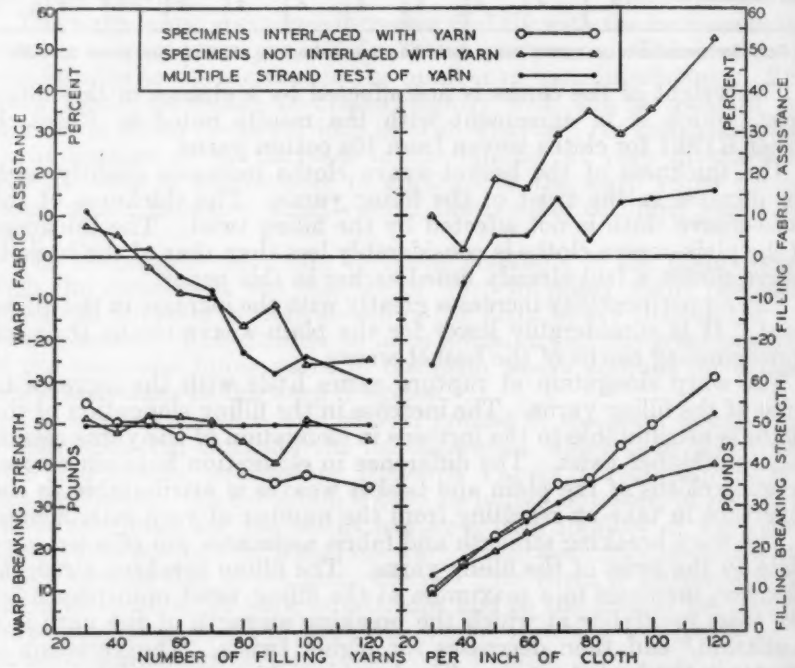

FIGURE 3.—*Breaking strength of cloth specimens woven from 2/140 mercerized cotton yarn, yarn specimens which had been subjected to the actions of the loom without interlacing with a second set of yarns, and original yarns tested by the multiple-strand method.*

The fabric assistance of the cloths is based upon the breaking strength of the yarns which had been subjected to the actions of the loom and upon the breaking strength of the yarns tested by the multiple strand method.

had been subjected to the actions of the loom and upon the breaking strength of the yarns tested by the multiple-strand method.

Loom abrasion decreases the breaking strength of the yarns in the cloth. The decrease is proportional to the amount of loom abrasion, that is, to the number of filling yarns per inch since the movements of the loom are directly proportional to the number of filling yarns per inch. This effect is clearly shown by the progressive decrease in the warp breaking strength of the cloths and in the breaking strength of the warp yarns which had been subjected to the actions of the loom with the increase in the number of filling yarns per inch. It is

also clearly shown by the progressive decrease in the breaking strength of the filling yarns which had been subjected to the actions of the loom relative to the breaking strength of the filling yarns tested by the multiple-strand method.

Fabric assistance increases with the number of yarn interlacings. This effect is clearly shown by the progressive increase in the filling breaking strength of the cloth relative to either the breaking strength of an equal number of filling yarns tested by the multiple-strand method, or to the breaking strength of the filling yarns woven across an area of the warp from which the warp yarns have cut out. The results for the warp indicate that loom abrasion decreases the warp breaking strength at a greater rate as the number of filling yarns per inch is increased than the increase resulting from the increase in the number of yarn interlacings. It should be noted, however, that the effects of these two opposing factors are equal at 50 filling yarns per inch. Below 50 filling yarns per inch the effect of the number of yarn interlacings is greater than loom abrasion as indicated by a positive fabric assistance. Above 50 filling yarns per inch the effect of loom abrasion is greater as indicated by a negative fabric assistance.

WASHINGTON, December 30, 1935.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP863

Part of Journal of Research of the National Bureau of Standards, Volume 16, February 1936

ELECTRICAL-RESISTANCE ALLOYS OF COPPER, MANGANESE, AND ALUMINUM

By James L. Thomas

ABSTRACT

An investigation has been made of the electrical properties of alloys containing from 4 to 15 percent of manganese and from 0 to 10 percent of aluminum, the remainder being copper. An alloy containing 85 percent of copper, 9.5 percent of manganese, and 5.5 percent of aluminum has properties very similar to those of manganin. Its thermoelectric power against copper is much smaller than that of manganin and this thermoelectric power may be brought to zero by the addition of a very small amount of iron. Resistance coils constructed from these alloys, with or without added iron, have been very stable in resistance. By properly baking, their temperature coefficients of resistance at 25° C may be made as nearly zero as is desired, and this coefficient changes less with temperature than does that of manganin.

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I. INTRODUCTION

The electrical properties of an alloy of copper, manganese, and aluminum have been under observation at the National Bureau of Standards since about 1910. At that time William B. Driver gave to this Bureau some samples of such an alloy, which he had developed as an electrical-resistance material. This material, which is of the type later called Therlo, had almost the same electrical properties as manganin, with the exception of its smaller thermoelectric power against copper. Chemical analyses of two samples of this alloy gave the following results: *sheet material*—copper, 84.35 percent; manganese 11.48 percent; aluminum, 4.2 percent; iron and nickel, traces; *wire*—copper, 84.05 percent; manganese, 11.54 percent; aluminum, 4.2 percent; and nickel, 0.12 percent.

Of the resistance standards constructed of these materials, two 10-ohm standards and a 0.01-ohm standard were kept under observation by Dr. Frank Wenner of this Bureau and in regular use for more

than 20 years. During that time the two 10-ohm standards increased in resistance, respectively, by 100 and 30 parts in a million, while the 0.01-ohm standard increased by 220 parts in a million. Judging by the appearance of the sheet material, Dr. Wenner concluded that the original ingot was probably not free from blow holes, and that an appreciable amount of the aluminum had been oxidized and therefore was not in solution. However, on the basis of the results obtained with these samples, he advocated a thorough investigation of copper-manganese-aluminum alloys in the hope of developing a more suitable material for use in the construction of resistance standards and coils than any of the materials then available.

With the expectation that modern methods of producing alloys containing aluminum would yield better results, experiments were begun recently upon the production of alloys of copper, manganese, and aluminum. After a considerable amount of experimentation a technique for the production of satisfactory alloys of this type was developed; and alloys containing from 0 to 10 percent of aluminum and from 4 to 15 percent of manganese, the remainder being copper, have been investigated. For use in the construction of coils for electrical-resistance standards and measuring apparatus, the best composition was found to be approximately 85 percent of copper, 9.5 percent of manganese, and 5.5 percent of aluminum. This alloy has nearly the same resistivity as manganin, its temperature coefficient of resistance at 25° C can be brought to zero by a suitable heat treatment, and the change of the temperature coefficient with temperature is about half that of manganin. Its thermoelectric power against copper at 25° C is only about 10 percent of that of manganin, and this thermoelectric power may be further reduced by the addition of a very small percentage of iron without materially affecting the other properties of the alloy. The stability of the electrical resistance of these alloys, with or without added iron, is apparently as good as that of manganin.

II. PREPARATION OF ALLOYS

The copper and aluminum used in preparing these alloys were of high quality, the total impurities not exceeding 0.03 percent in either material. Unfortunately, the manganese available was not of a comparable purity. It was Standard Sample 67 of this Bureau, containing 97.25 percent of manganese, by analysis. The principal impurities were iron, 1.5 percent; silicon, 0.4 percent; and phosphorus, 0.2 percent. In weighing out the ingredients for these alloys, no allowance was made for the impurities. Hence, in what follows, unless otherwise stated, the percentage of any ingredient includes that of its impurities.

The alloys were prepared in Acheson graphite crucibles which were heated by means of an induction furnace. The copper was first melted in the crucibles under a heavy coating of cryolite (Na_3AlF_6 or $3NaF{\cdot}AlF_3$), a flux in which aluminum oxide is soluble. The manganese, in granular form, was then added, and finally the aluminum. The addition of the aluminum resulted in a considerable rise in temperature, so the induction furnace was then cut off and the charges were thoroughly stirred with graphite rods, and poured into graphite molds.

To obtain some idea of the losses during the melting and working into wire, a chemical analysis of one sample was made. The alloy selected for this analysis had been worked into wire 0.53 mm in diameter, and the composition, as calculated from the chemical analyses of the ingredients, was: copper, 84.92 percent; manganese, 9.24 percent; aluminum, 5.50 percent; iron, 0.22 percent; and impurities, 0.12 percent. The chemical analysis of the finished wire showed: copper, 85.2 percent; manganese, 9.2 percent; aluminum, 5.2 percent; iron, 0.20 percent; remainder, 0.2 percent. The difference between

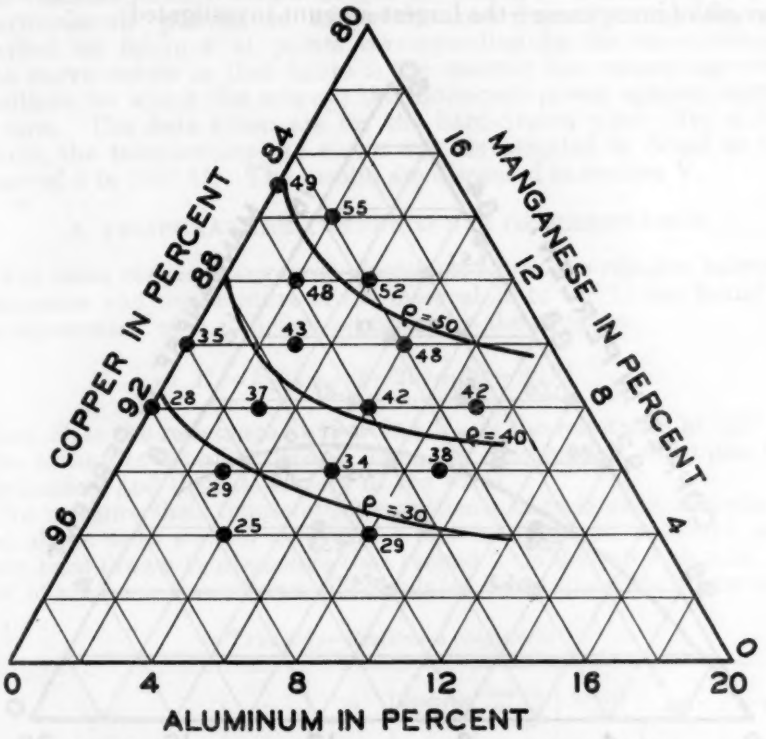

FIGURE 1.—*Resistivities of copper-manganese-aluminum alloys.*

The resistivities are for hard-drawn wires at 25° C and are expressed in microhm-centimeters. The compositions shown were calculated from the weights of the impure ingredients.

the chemical analysis and the calculated composition could be almost entirely explained by the assumption of a loss in aluminum amounting to 0.3 percent of the weight of the alloy. Such a loss of aluminum is entirely possible, as aluminum would probably reduce any oxide present as well as remove any oxygen dissolved in the molten alloy.

The ingots were heated in air and hot-forged into the form of rods 5 or 6 mm square. They were then cold-rolled and swaged into wire about 1 mm in diameter, after which they were drawn through steel dies to a diameter of about 0.5 mm. The material was annealed several times during the rolling and swaging, but the wire was not annealed during the drawing. In annealing, the material was heated

only to a dull red, as higher temperatures would sometimes produce a hardening. The wire was not pickled to remove the oxide from the surface, but at the beginning of the drawing its surface was carefully cleaned with sandpaper.

The difficulty of working the alloys into wire was found to increase with the percentage of aluminum. No alloy containing more than 9 percent of aluminum was worked into wire, although an ingot containing 10 percent of aluminum and 10 percent of manganese was worked down sufficiently to get an estimate of its resistivity. No difficulty was encountered in handling ingots containing up to 15 percent of manganese—the largest amount investigated.

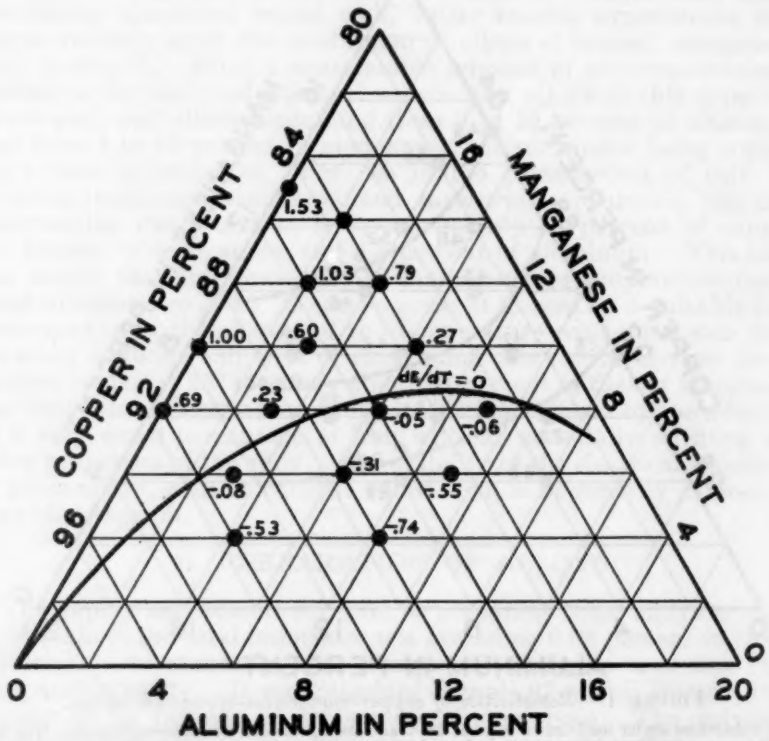

FIGURE 2.—*Thermoelectric power against copper of hard-drawn wire of copper-manganese-aluminum alloys.*

Average thermoelectric powers from 0 to 100° C, in microvolts per degree C.

III. ELECTRICAL PROPERTIES

1. RESISTIVITY

After the alloys had been worked into wire about 1 mm in diameter, their resistivities were measured. These were determined for the cold-worked wire, and the results are shown in figure 1. In this figure the resistivities in microhm-centimeters are marked at the points that represent the compositions on the three-phase diagram. Contour lines have been drawn connecting compositions having the same resistivities. These resistivities apply only to the cold-worked

wire, as there was a considerable change when the wires were annealed, amounting in some cases to over 10 percent.

2. THERMOELECTRIC POWER

To measure their thermoelectric powers against copper, pieces of the wire were soldered to copper wires. One junction was kept at the temperature of ice and the other at steam, and the emf were measured with a low-resistance Diesselhorst potentiometer. For most of the alloys only this one temperature interval was used, so the values obtained were averages between 0 and 100° C. These thermoelectric powers, in microvolts per degree centigrade, are marked on figure 2 at points corresponding to the compositions. The curve shown in that figure is the contour line connecting compositions for which the average thermoelectric power against copper is zero. The data given are for the hard-drawn wire. For a few alloys, the temperature-emf curve was investigated in detail in the interval 0 to 100° C. The results are discussed in section V.

3. TEMPERATURE COEFFICIENTS OF RESISTANCE

For these copper-manganese-aluminum alloys the relation between resistance and temperature in the interval 20 to 30° C was found to be represented with sufficient accuracy by the equation:

$$R_t = R_{25}[1+\alpha(t-25)+\beta(t-25)^2].$$

Here, R_t is the resistance at t° C and R_{25} is the resistance at 25° C. The constants α and β depend upon the composition and upon the mechanical and thermal history of the wires.

To measure their temperature coefficients of resistance, samples of the alloys were worked into wire 1 mm in diameter, annealed, and then hard-drawn to diameters that ranged from 0.43 to 0.55 mm. A coil of each was wound on a silk-insulated brass spool, the turns were

TABLE 1.—*Resistance coefficients*

Alloy	Mn	Al	Diameter of wire	Baking temperature	Baking time	$\alpha \cdot 10^6$	$\beta \cdot 10^6$
	%	%	mm	°C	hr		
A	4	4	0.43	140	18	124	0.00
B	4	8	.46	140	18	151	.00
C	6	3	.43	140	18	52	−.14
D	6	6	.43	140	18	57	−.08
E	6	9	.56	140	18	76	−.08
F	8	0	.48	140	18	45	−.46
G	8	3	.43	140	18	12	−.24
H	8	6	.46	140	18	6	−.14
J	8	9	.53	140	18	55	−.28
K	10	0	.51	140	18	20	−.58
L	10	3	.46	140	12	−13	−.22
M	10	6	.56	140	18	−15	−.22
P	11	0	.56	140	48	22	−.54
Q	12	2	.48	140	18	−21	−.42
R	12	4	.48	140	18	−33	−.26
S	12	6	.56	140	18	−24	−.30
T	14	2	.48	140	18	−24	−.42
U	15	0	.56	140	18	30	−.90

separated with silk thread, and the coils were shellacked, and all but two were baked for 18 hours at 140° C. The coils were then adjusted to have a resistance of 10 ohms, and their resistances were measured in oil baths at 20, 25, and 30° C. For these measurements a bridge was used with which a precision of a part in a million was easily attained for the resistance measurements. The results are given in table 1.

The values of α, in parts per million per degree centigrade, (ppm/°C) are marked on the 3-phase composition diagram shown in figure 3.

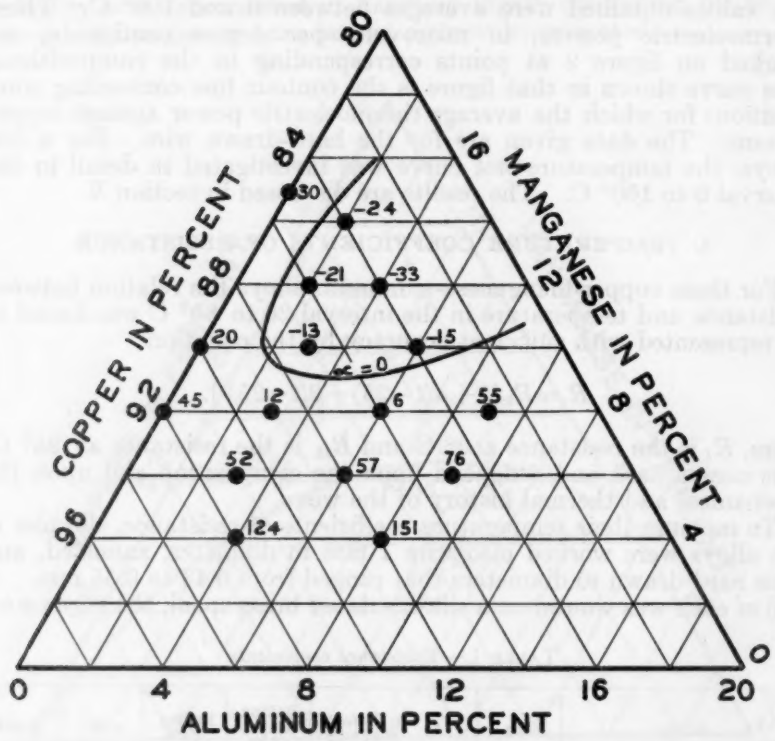

FIGURE 3.—*Values of α at 25° C for hard-drawn wire after baking at 140° C for 18 hours, in parts per million per degree C.*

The contour line shows a series of alloys for which the value of α, that is, the slope of the resistance-temperature curve at 25° C, is zero. As pointed out above, these values of α were determined after the wires were baked at 140° C. This baking produced a considerable decrease in the resistance, and at the same time an increase in the temperature coefficient. The decrease in resistance amounted to as much as 8 percent for coils baked at 140° C, and was roughly proportional to the aluminum content. The change in the value of α was of the order of 2 or 3 ppm/°C for each 1-percent change in resistance. The baking of the coils was intended primarily to increase the stability of their electrical resistance.

The values of β in parts per million per °C per °C are shown in figure 4. Contour lines for equal values of β are shown, but their locations are somewhat uncertain as the data were not entirely consistent. No values of β were obtained for the unbaked wire, so it is not known how its value depends upon the baking. However, all but one of several coils annealed at about 500° C had larger numerical values for β than did coils of the same material baked at 140° C. This was not necessarily a result of the difference in heat treatment, as the wires annealed at the higher temperature were of a larger diameter.

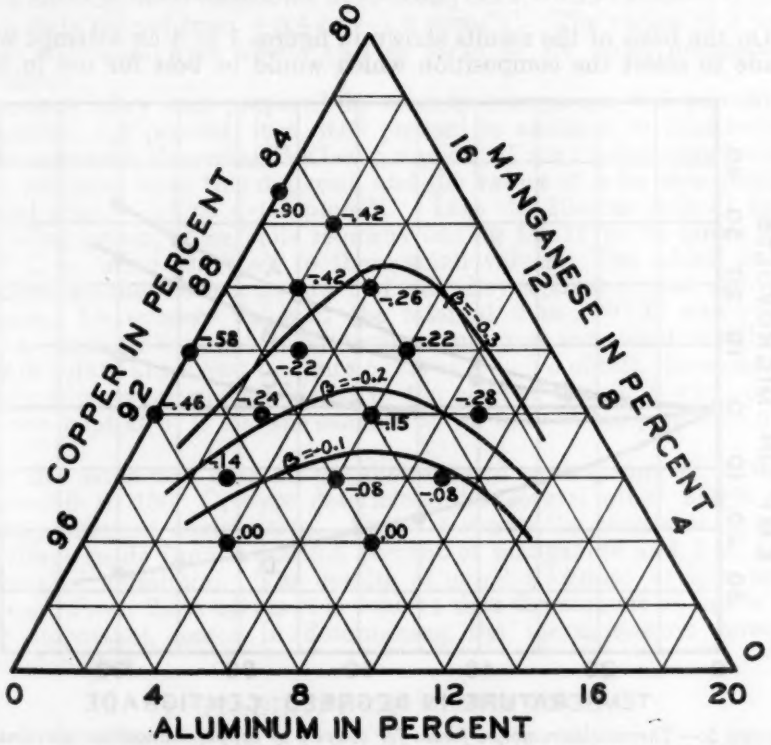

FIGURE 4.—*Values of β in parts per million per °C per °C for temperatures at or near 25° C.*

These values are for hard-drawn wire after baking for 18 hours at 140° C.

IV. EFFECT OF IMPURITIES

The principal impurity in the alloys was iron which came from the manganese used in their preparation. To test the effect of iron an alloy was prepared, containing about 9.5 percent of manganese and 5 percent of aluminum, the remainder being copper. Calculated from the manganese used, the iron amounted to 0.15 percent. Part of this alloy was remelted and electrolytic iron was added to raise the iron content to 0.30 percent. This additional iron raised the resistivity from 45 to 45.5 microhm-centimeters, and decreased the thermoelectric power against copper from +0.3 to −0.3 μv/°C.

The alloy of 90 percent of copper and 10 percent of manganese was also melted with additional iron. The iron content of this alloy was increased by about 0.3 percent, and this resulted in an increase in the resistivity from 35 to 36.5 microhm-centimeters. At the same time the thermoelectric power against copper was decreased from 1.0 to 0.2 μv/°C.

The effect of impurities other than iron was not investigated. It it assumed that their effect is less than that of iron as they are presens in considerably smaller proportions.

V. BEST COMPOSITION FOR RESISTANCE COILS

On the basis of the results shown in figures 1 to 4 an attempt was made to select the composition which would be best for use in the

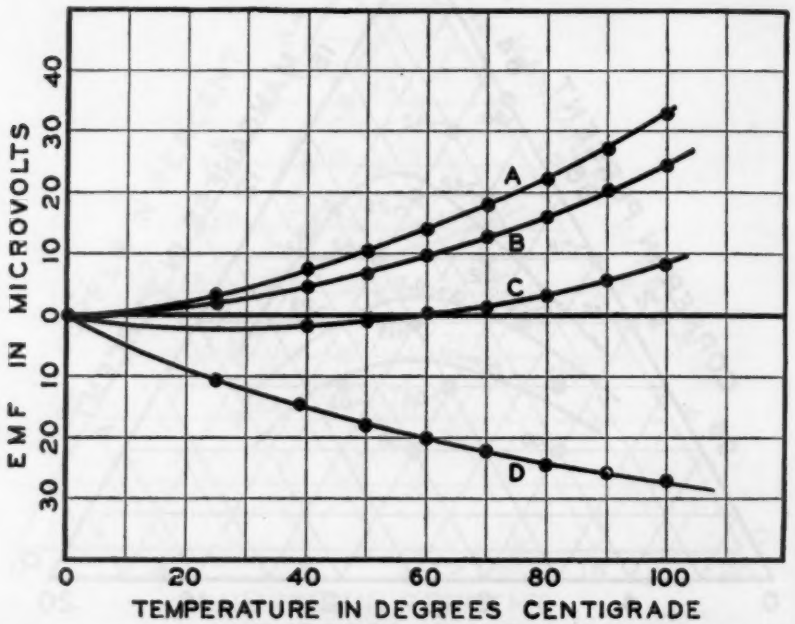

FIGURE 5.—*Thermoelectromotive forces for couples of copper-manganese-aluminum alloys, with and without added iron, against copper.*

These curves were obtained by keeping one junction at 0° C and bringing other junctions to temperatures as shown on plot. Curves are for alloys of following ingredients, besides copper:

Curve	Manganese	Aluminum	Iron
	%	%	%
A	9.5	5.5	0
B	9.0	5.0	0
C	9.5	5.5	0.07
D	9.5	5.0	0.15

construction of coils for resistance standards and for measuring apparatus. When the curves of figures 2 and 3 are drawn on the same diagram they do not intersect. It was, therefore, not possible to obtain an alloy of these three ingredients having both a zero temper-

ature coefficient of resistance at 25° C and a zero thermoelectric power against copper. Hence the composition was selected which would give an alloy with a zero temperature coefficient and the smallest obtainable thermoelectric power against copper. For this purpose the following composition was chosen: copper, 85.5 percent; manganese, 9.5 percent; and aluminum, 5 percent. This is the alloy described in section IV for which the resistivity was 45 microhm-centimeters and the average thermoelectric power against copper was $+0.3$ μv/°C for the interval 0 to 100° C. Three 10-ohm resistance standards were made of coils of this wire and baked until their temperature coefficients of resistance were nearly zero. The values of α for these coils ranged from $+0.4$ to -1.0 ppm/°C. The values of β for these standards were about half as large as for most manganin standards.

Another alloy was prepared to contain manganese, 9.5 percent; aluminum, 5.5 percent; iron, 0.07 percent in addition to that from the manganese; the remainder being copper. Four 10-ohm standards were prepared from this material, and the values of α for this group ranged from -0.1 to $+1.4$ ppm/°C. Like the 10-ohm coils of the preceding group, these coils required baking for 18 to 24 hours at 140° C to bring their α's to these small values. The added iron brought the thermoelectric power of this alloy against copper almost to zero. Its average value in the interval 0 to 100° C was 0.08 μv/° C, and its value at room temperature was somewhat smaller. Detailed data are shown in figure 5, curve C. To obtain these data, copper wires were silver-soldered to the ends of the alloy wire, one end was kept at 0° C and the other in an oil bath at temperatures up to 100° C.

In this same way data on the thermal emf against copper, in the interval 0 to 100° C, were determined for several other alloys of slightly different composition. Figure 5 shows the results obtained for alloys made from 9 and 9.5 percent of manganese and 5 or 5.5 percent of aluminum. The results of small additions of iron are shown. From these curves it is evident that the amount of iron is a very important factor in determining the thermoelectric power against copper.

VI. STABILITY OF RESISTANCE

The stability of the electrical resistance of the copper-manganese-aluminum alloys has been tested for standards prepared in two ways. In the first place, the seven 10-ohm coils described in section V were sealed in oil-filled containers of the Rosa[1] type soon after their completion, and their resistances measured from time to time. Then three 1-ohm coils and one 10-ohm coil were annealed in vacuo at 475 to 550° C, and sealed in containers of the double-walled type.[2] The data obtained for these two groups of coils are given in tables 2 and 3. In addition to these coils, some 100-ohm and some 1-ohm coils have been recently constructed and baked at 140° C. While they have been under observation for only a short time, their initial performance has been about the same as for the 10-ohm coils which were baked at the same temperature.

[1] E. B. Rosa, Bul. BS 5, 413 (1908) S107.
[2] J. L. Thomas, BS J. Research 5, 295 (1930) RP201.

TABLE 2.—*Data on resistance coils baked in air at 140° C*

Items	Data for coils numbered—						
	1	2	3	4	5	6	7
Copper (%)	85.5	85.5	85.5	84.93	84.93	84.93	84.93
Manganese (%)	9.5	9.5	9.5	9.5	9.5	9.5	9.5
Aluminum (%)	5.0	5.0	5.0	5.5	5.5	5.5	5.5
Added iron (%)	0.0	0.0	0.0	0.07	0.07	0.07	0.07
Diam of wire (mm)	0.56	0.56	0.56	0.53	0.53	0.53	0.53
Baking temp (°C)	140	140	140	140	140	140	140
Baking time (hr)	18	24	18	42	18	18	24
$\alpha \cdot 10^6$/°C	0.4	−1.0	−1.0	0.0	1.4	1.3	−0.1
$\beta \cdot 10^6$/°C^2	−0.20	−0.20	−0.24	−0.24	−0.24	−0.22	−0.22
Date	**Resistance at 25° C, in ohms**						
1935							
March 29	9.99482						
April 4	9.99484						
April 18	9.99485			9.99524			
May 2	9.99486	9.99548	9.99531	9.99528	9.99563	9.99534	9.99532
May 24	9.99487	9.99579	9.99540	9.99528	9.99564	9.99537	9.99536
June 24	9.99489	9.99582	9.99544	9.99530	9.99564	9.99540	9.99539
July 23	9.99487	9.99581	9.99545	9.99529	9.99562	9.99538	9.99539
August 23	9.99488	9.99582	9.99548	9.99529	9.99563	9.99537	9.99541
October 9	9.99487	9.99580	9.99548	9.99528	9.99563	9.99536	9.99541
November 8	9.99487	9.99581	9.99552	9.99530	9.99564	9.99537	9.99542

TABLE 3.—*Data on resistance coils annealed in vacuo at about 500° C*

Items	Coil number—			
	1	2	3	4
Copper (%)	87	87	82	86
Manganese (%)	10	10	12	9
Aluminum (%)	3	3	6	5
Diam of wire (mm)	0.65	1.25	1.7	1.4
Annealing temp (°C)	475	500	550	550
$\alpha \cdot 10^6$/°C	9.4	8.3	12.1	31.0
$\beta\ 10^6$/°C^2	−0.24	−0.30	−0.28	−0.26
Date	**Resistance at 25° C, in ohms**			
1935				
February 11	9.99557			
February 25	9.99557	0.999572		
March 11	9.99555	.999571		0.999477
March 25	9.99553	.999570	0.999548	.999475
April 22	9.99555	.999569	.999547	.999474
May 22			.999546	.999473
June 25	9.99556	.999569	.999546	.999474
August 23	9.99557	.999568	.999545	.999473
October 9	9.99557	.999566	.999546	.999473
November 8	9.99557			

So far the coils baked at 140° C have been as stable or more stable in resistance than manganin coils prepared in the same way. The coils annealed in vacuo at 475 to 550° C have performed very much like manganin coils baked at 550° C and sealed in double-walled containers. The latter generally change by 2 or 3 ppm during the first month after sealing.

VII. MISCELLANEOUS PROPERTIES

It was hoped that the presence of aluminum in these alloys would make them nontarnishing. This, however, was found not to be the case. They discolored rather rapidly even when exposed to air at atmospheric temperatures. A very decided darkening of the surface was produced by baking at 140° C for a few hours. However, it is possible that this oxidation forms a surface coating which retards further surface action.

After being severely cold-worked the alloys were very strong and springy. However, when baked at 140° C for 18 hours, alloys containing 9.5 percent of manganese and 5 to 6 percent of aluminum were found to be very brittle, and the wire would break when it was bent sharply. The ductility could be restored by annealing in a gas flame. No tests were made of the other alloys to see if they also became brittle from baking.

The temperature coefficient of linear expansion was measured for one sample of the alloy made to contain 84.93 percent of copper, 9.4 percent of manganese, 5.5 percent of aluminum, 0.15 percent of iron from the manganese, and 0.07 percent of added iron. A piece of this material was cold-drawn from 1 mm down to 0.5 mm and baked in air at 140° C for 18 hours. Its coefficient of expansion was then determined from measurements at 20 and 100° C, and its average value in this interval was found to be 0.000 018 per degree centigrade. This value is practically the same as that reported by A. Schulze [3] for manganin, and it is also very near to that of the brass spools on which resistance coils are ordinarily mounted.

The 10-ohm coils of the alloy having the best composition were made from wire which was annealed at a diameter of 1 mm and then cold-drawn to a diameter of about 0.5 mm. Such coils required a baking of about 18 hours at 140° C to obtain the desired temperature coefficient of resistance. However, when a piece was cold-drawn from 1 to 0.2 mm, in order to obtain wire for a 100-ohm coil, a longer baking was required. Two 100-ohm standards prepared in this way had to be baked for 72 hours at 140° C in order to obtain the desired small temperature coefficients. It follows that the amount of baking required to bring the temperature coefficient to zero depends upon the amount of cold-working to which the wire has been subjected. The time of baking has not been investigated for wires of other diameters.

The author wishes to express his thanks to J. A. Scherrer for the chemical analysis of one of these alloys and to P. Hidnert for the determination of its temperature coefficient of linear expansion.

WASHINGTON, December 12, 1935.

[3] Z. tech. Phys. **14**, 89 (1933).

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ACTION OF "HYPO" SOLUTION ON STONE TANKS

By Daniel W. Kessler

ABSTRACT

The resistance of five types of natural stone to "hypo" solutions has been studied under conditions simulating those in hypo tanks. For stones of high resistance to acid attack, the destructive action is mainly physical and is caused by the salts crystallizing in the pores of the stone above the solution level. The resistance of the samples was studied in relation to certain physical properties, and a specification is suggested which would probably obtain suitable stone for hypo tanks.

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I. INTRODUCTION

The destructive action of hypo solutions on tanks is well known to operators of photographic shops. Wood and some varieties of natural stone have been commonly used for large hypo tanks, but apparently the same kind of destructive action occurs on both materials. One case has been noted in which a stone tank was in an advanced state of disintegration after 3 years of service. Another case, in which a different variety of stone was used, shows reasonably good service, as the tank has been in use for 18 years. Three sides of this tank have deteriorated considerably, and one is still in good condition.

The tanks are usually filled about half full of the solution, which penetrates into the pores of the stone, and crystals of the salts may form from the liquid level to the top of the tank because the solution is drawn upward by capillarity. In the denser stones this crystallization manifests itself by a narrow band of spalling slightly above the solution, but in more porous materials the spalling may cover a larger area and even extend to the top. The spalling is usually more prominent on the inside of the tank, but it sometimes occurs on the outside also. Laboratory studies were undertaken to determine those properties of stone conducive to longer service and those which must be avoided. The solution contains acetic acid, and consequently calcareous materials should not be used. However, the difficulty is not

necessarily one of securing a stone chemically resistant to hypo solution, since the destructive action is caused mainly by the salts crystallizing in the pores of the stone and creating sufficient pressure to cause spalling.

II. STONE SAMPLES

Five types of stone were selected for study, as follows: (1) talcose serpentine; (2) chloritic amphibole; (3) slate; (4) bluestone; and (5) soapstone.

The talcose serpentine has been used to a considerable extent for hypo tanks and some grades have given good service. Type (2) has had only a limited use in hypo tanks and, in one case at least, the results were unsatisfactory.

Types (3), (4), and (5) were included because they can be readily worked into suitable shapes for tank construction. Seven samples of talcose serpentine, nine of chloritic amphibole, two of bluestone, two of slate (one blue-gray and one green), and one of soapstone were exposed to the hypo solution. Cleavage was most pronounced in the slate, much less so in the bluestone, least in the chloritic amphibole, and absent in the serpentine and soapstone samples. Other physical properties of the various samples are given in table 1. The slates gave the highest strengths when tested perpendicular to the cleavage

TABLE 1.—*Physical properties and ratings of materials*

Designation	Classification	48-hr. absorption [1]	Abrasive hardness, [2] (H^a)	Modulus of rupture [3]	Bulk density	Observed condition after test [4]
		Weight (%)		lb/in²		
A_1	Bluestone	2.9	14.0	2,000	2.47	e
A_2	do	2.5	13.6	4,000	2.47	d
B_1	Chloritic amphibole	.18	16.2	[5] 680	2.99	d
B_2	do	.18		3,500	2.97	d
B_3	do	.14	7.8	2,680	2.94	c
B_4	do	.18	10.8	6,240	2.97	c
B_5	do	.18	12.6	3,640	2.98	c
B_6	do	.15	35.2		2.97	c
B_7	do	.22	10.8	6,240	2.96	c
B_8	do	.17	12.0	2,490	2.96	c
B_9	do	.15	12.0	5,900	2.94	c
C_1	Slate	.35	7.0	11,500	2.78	d
C_2	do	.12	7.7	10,800	2.79	b
D_1	Talcose serpentine	.20	4.5	2,400	2.87	c
D_2	do			2,380		c
D_3	do	.06	19.5	2,850	2.96	a
D_4	do	.07	18.9	5,680	2.95	a
D_5	do	.07	32.1	6,120	2.85	a
D_6	do	.09	39.9	4,450	2.87	a
D_7	do	.20	4.5	1,840	2.87	d
E	Soapstone	.14	4.0	1,920	3.13	c

[1] *Absorption test.*—Specimens approximately 2 by 2 by 1 in. were dried at 105 ±2° C for 24 hours, allowed to cool for 30 minutes, weighed, then immersed in water at approximately 20° C for 48 hours. The final weights were determined after drying the surfaces of the specimens with a towel. The absorption values are expressed in percent by dividing the weight of water absorbed times 100 by the dry weight of the specimen.

[2] *Abrasive hardness.*—The tests were made on specimens measuring approximately 2 by 2 by 1 in. The apparatus and procedure are described in National Bureau of Standards Research Paper RP612, Wear Resistance of Natural Stone Flooring.

[3] *Flexure test.*—Specimens approximately 12 by 2 by 1 in. were supported flatwise on knife-edges of the rocker type, spaced 10 in., on centers. Loads were applied through a third knife-edge at the center of span until rupture occurred. The modulus of rupture, R, was computed by means of the formula: $R=3/2\ (wl/bd^2)$, where w=load in pounds causing rupture; l=span, in inches (distance between supporting knife-edges); b=width of specimen, in inches; and d=thickness of specimen, in inches.

[4] Samples showing no definite deterioration are rated "a", those showing the greatest amount "e." Others are given intervening letters in accordance with their observed condition.

[5] Sample B was tested parallel to the cleavage. All other samples were tested perpendicular to the cleavage.

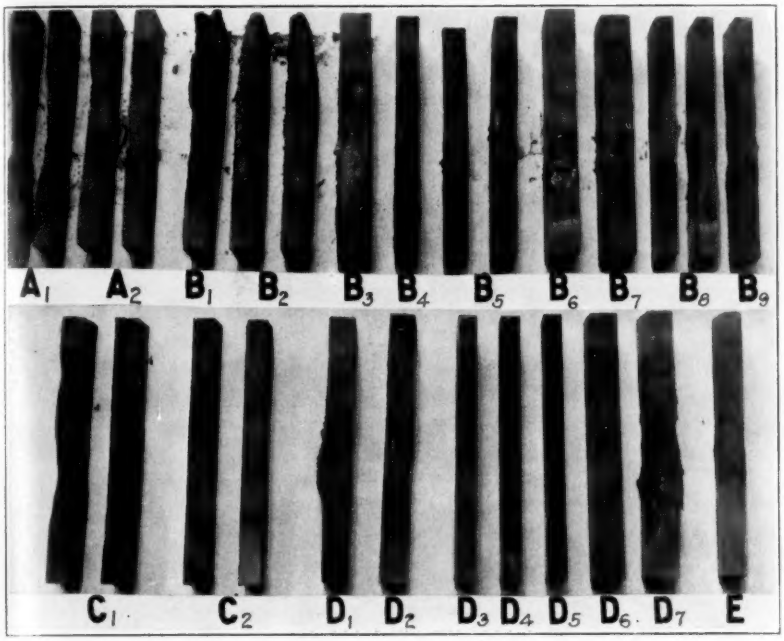

FIGURE 1.—*Specimens of stone after exposure for 18 months to hypo solutions.*

Sample number	Material
A_1 and A_2	Bluestone.
B_1 and B_9	Chloritic amphibole.
C_1 and C_2	Slate.
D_1 to D_7	Talcose serpentine.
E	Soapstone.

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plane but if they had been broken along the cleavage plane, the values would have been very low. One chloritic amphibole sample (B_1, table 1) was broken in the cleavage direction, and the strength was shown to be low.

III. DESCRIPTION OF TESTS

The experiments were made on specimens measuring approximately 12 by 2 by 1 in. All specimens having definite cleavage were cut with the cleavage plane parallel to the long dimension except three of the chloritic amphibole specimens (two of B_5 and one of B_8), which were cut with the cleavage perpendicular to the long dimension. The specimens were placed on end in glass vessels in which a depth of about 4 in. of hypo solution was maintained. This exposure was intended to simulate the condition in hypo tanks. The hypo solution used in photographic shops is as follows:

Solution A:
1 part of sodium thiosulphate.
4 parts of water.
Solution B:
360 grams of sodium sulphite.
315 grams of glacial acetic acid.
360 grams of potassium alum.
Add water enough to make 4 liters.

One part of solution B is added to eight parts of solution A. Since the hypo solution in actual use becomes contaminated with silver halides from the developed photographic emulsion, the solution used in the tests was made up of one part of used solution, taken from a tank in the photographic shop, and two parts of freshly made solution.

The conditions of the test are believed to have been more severe than those in service, because the specimens could absorb the solution from five faces, while in tanks only one face is exposed to the solution. As some of the specimens had prominent cleavage the test conditions for such materials were more severe than for materials without cleavage, because absorption may occur more freely in the cleavage direction.

IV. RESULTS OF TESTS

Within a short time the salts from the hypo solution formed incrustations on the specimens above the liquid level. After 6 months the bluestones were crumbling at the corners to a depth of about one-fourth inch and to a slight depth on the cleavage faces. The dark-colored slate developed cracks along the cleavage planes. After 12 months the bluestone, dark slate, and some of the chloritic amphibole specimens were in an advanced state of decay. The bluestones failed by flaking and crumbling, which occurred from the solution level upward for about 4 in. The dark slates showed two types of disintegration, one which caused the specimens to split along the cleavage, and the other which loosened splintery fragments from the corners and cleavage faces. The green slates showed only a small amount of scaling, while most of the chloritic amphibole specimens flaked on their cleavage faces, and some of the talcose serpentines scaled to an appreciable depth.

The test was discontinued at the end of 18 months, at which time all specimens, except four talcose serpentines (D_3, D_4, D_5, and D_6), showed definite disintegration. The final condition is illustrated in

figure 1, and a rating based on the relative amount of disintegration is given in table 1. Samples showing no definite deterioration are rated "a", and those showing the greatest amount "e". Others are given intervening letters in accordance with their observed conditions.

V. CONCLUSIONS

The physical property of stone which appears to be most determinative of resistance to hypo solutions is porosity. All of the samples rated "a" and "b" have absorption values of 0.12 percent, or less.

Abrasive hardness seems to have no effect on the resistance to disintegration, but it might be desirable, from other points of view, to employ hard materials, as they would be less apt to become scratched or worn.

Although the results do not show a definite relation between strength and resistance, this may be due to the fact that strength values were determined in only one direction for each sample. Except in the case of the green slate, all samples having cleavage effects showed poor resistance to hypo solution. Since this slate had a much less pronounced fissility than the dark slate, it may be inferred that a high flexural strength may offset, to some extent, the effects of cleavage.

Based on the results of this study, the following quality specification is suggested for stone hypo tanks: The stone shall be highly resistant to acids and free from cleavage; the flexural strength (modulus of rupture) shall be not less than 2,800 lb/in.^{2}; and the absorption shall be not more than 0.12 percent. Obviously this specification would not admit slate on account of its cleavage. If the degree of fissility could be measured it might be possible to formulate a specification which would obtain slate, such as C_2, giving good service in hypo tanks.

WASHINGTON, December 27, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP865

Part of Journal of Research of the National Bureau of Standards, Volume 16, February 1936

NOTE ON THE GUARDED-FIELD X-RAY IONIZATION CHAMBER

By Lauriston S. Taylor and George Singer

ABSTRACT

The number of guard wires in the NBS guarded-field ionization chamber has been reduced from twelve to eight, and the other attendant alterations necessitated thereby are given. It is shown that strictly uniform potential distribution between guard wires is not essential and that ionization between guard wires, therefore, produces no spurious effects within the chamber. Coin-gold diaphragms have replaced those used prior to 1931. Coplanarity of electrodes is assured by making them as a single unit.

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I. NUMBER OF GUARD WIRES

The rather extensive adoption of the Bureau's design of an X-ray ionization chamber [1] makes it desirable to describe some minor improvements made since publishing the description; and, at the same time, to clear up some misapprehensions as to the adequacy of the particular design of chamber which has been chosen. For instance, two cases have come to our attention in which an insufficient knowledge of the theory [2] of the guarded-field chamber has led to errors of 2 or 3 percent. On the other hand, out of a number of such chambers calibrated in this laboratory, only one has been found in error by an amount substantially greater than that fixed by the experimental tolerances.

When preparing to make an international comparison of standards in 1931, we reduced the number of guard wires from the previous selection of twelve to eight.[3] This was principally for use in European

[1] Lauriston S. Taylor and George Singer, BS J. Research 5, 507 (1930) RP211.
[2] C. Snow, BS J. Research 1, 513 (1928) RP17.
[3] Lauriston S. Taylor, BS J. Research 8, p. 9 (1932) RP397. This particular 8-wire chamber has been preserved intact for a reference standard.

laboratories to facilitate the alignment of the chamber in the radiation beam. From the theory of the guarded field, this change called for a lengthening of the lead box surrounding the plate system, in order to retain field disturbance at the center of the chamber within the desired limits.

Figure 1 shows a plot of the measured ionization current, using the 8-wire chamber, as a function of the spacing between the guard wires and end plates. It is evident that the field disturbance effectively disappears with the spacing greater than 5 cm. As a safety margin,

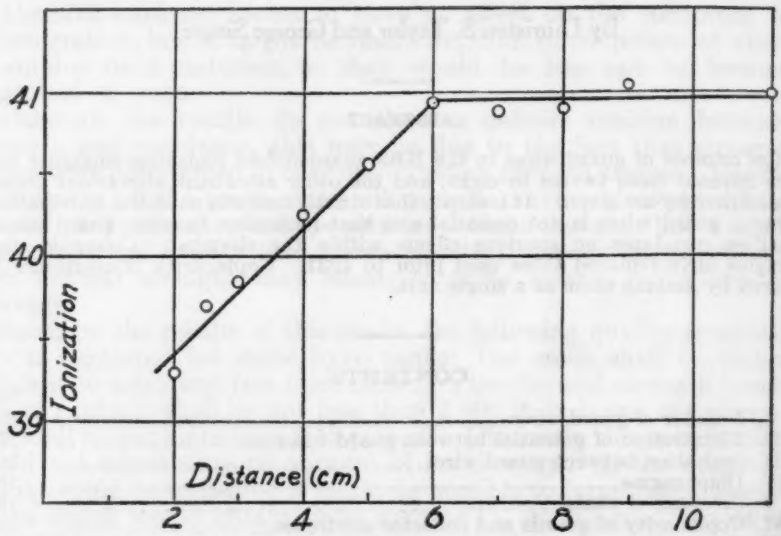

FIGURE 1.—*Measured ionization current as a function of the spacing between the guard wires and the grounded case.*

there is always employed a 7-cm spacing on the 8-wire chambers, whereas a 4-cm spacing had been found sufficient on the 12-wire chambers.

Similar studies were made with a guarded-field chamber designed for low-voltage radiations (4 to 90 kv)[4] having 4 guard wires 1 cm apart. In that case, a separation of 3 cm between guard wires and end plates was found sufficient.

II. DISTRIBUTION OF POTENTIAL BETWEEN GUARD WIRES

It has been found by trial that exactly equal potential differences from one guard wire to the next is not strictly necessary. Figure 2 shows a plot of the measured ionization current as the potential difference between the central pair of guard wires is changed from 0 to 2 times its normal value in the 8-wire chamber. In this, it is seen that

[4] L. S. Taylor and C. F. Stoneburner, BS J. Research 9, 769 (1932) RP505.

a difference of ± 3 percent from the normal potential difference causes a change of 0.1 percent in the measured ionization current. It is, of course, a very simple matter to maintain the potential distribution between guard wires to within 0.5 percent of the normal value. When using graphite or similar resistors in the potential divider, it is necessary only that their resistance remain very constant during a single determination.

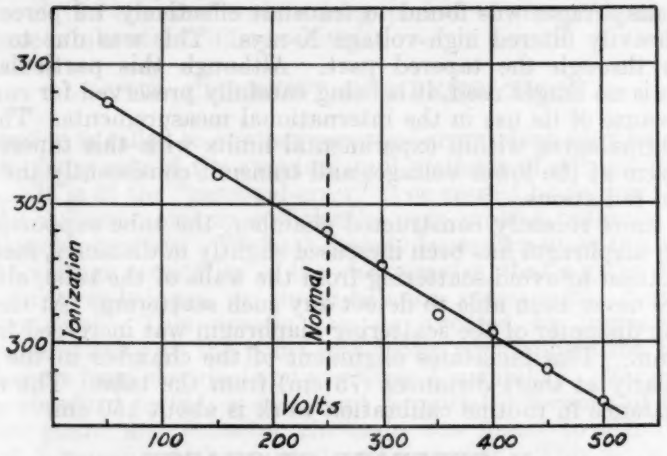

FIGURE 2.—*Measured ionization current as a function of the potential difference between the central pair of guard wires.*

III. IONIZATION BETWEEN GUARD WIRES

It has been suggested [5] that the relatively intense ionization between the central pair of guard wires might be a possible source of difficulty in a guarded-field ionization chamber. Such localized ionization can have two effects—one to introduce a slight further transverse inhomogeneity in the ion density about the defined X-ray beam, and the other to cause an effective change of resistance between the central guard wires, thus disturbing the field within the chamber. The matter of uneven ion density is of no importance for ordinary radiation intensities, provided that air absorption is negligible, since the measured ionization current is solely a function of the radiation flux density at the limiting diaphragm.[6] Since the resistance between successive guard wires is conveniently chosen at 0.2 to 0.5 megohm, the change in effective resistance due to the air conductivity is less than 0.001 percent. However, as noted above, the field at the center of the chamber is very insensitive to changes up to 5 percent in the guard-wire potentials and hence field disturbance caused by ionization between wires is negligible.

IV. DIAPHRAGMS

Following the international comparison, our chambers have been fitted with coin-gold (90 Au, 10 Cu) limiting diaphragms. This was

[5] W. V. Mayneord, Brit. J. Rad. **6**, 205 (1933).
[6] L. S. Taylor, BS J. Research **3**, 807 (1929) RP119.

decided upon when it was found that lead or lead alloy diaphragms could neither be made nor measured with sufficient accuracy. The gold diaphragms,[7] which are 4 mm thick, have been found to transmit through their boundary walls less than 0.1 percent of a heavily filtered 195-kv beam of radiation passing normally through the 8-mm aperture. In making the international comparisons, a slightly tapered lead-cadmium alloy diaphragm was used. As compared with the effective cross section of the aperture at low voltage, the tapered wall of this diaphragm was found to transmit effectively 1.2 percent too much heavily filtered high-voltage X-rays. This was due to transmission through the tapered part. Although this particular diaphragm is no longer used, it is being carefully preserved for comparison, because of its use in the international measurements. The gold diaphragms agree within experimental limits with this tapered-wall diaphragm at the lower voltages and transmit consistently the entire range of radiations.

In a more recently constructed chamber, the tube supporting the limiting diaphragm has been increased slightly in diameter, merely as a precaution to avoid scattering from the walls of the tube, although we have never been able to detect any such scattering. At the same time the diameter of the scattering diaphragm was increased from 12 to 14 mm. This facilitates alignment of the chamber in the beam, particularly at short distances (75 cm) from the tube. The normal tube distance in routine calibration work is about 150 cm.

V. CREEPAGE OF CHARGE

In the chambers now used, the potential dividing resistances are mounted on a hard-rubber panel just above the guard wires. When using a very sensitive detector system of low capacitance (FP–54, electrometer tube, 15 $\mu\mu$f), we have occasionally been troubled by charges induced on the collector electrode, apparently from creepage along the rubber surface. This usually arises in damp weather, but might be avoided by a different mounting of the resistors.

VI. COPLANARITY OF GUARDS AND COLLECTOR ELECTRODES

Another source of error has been found to lie in the failure to secure perfect alignment in the same plane of the guard and collector electrodes. To avoid this, these three electrodes have been mounted in a separate rigid unit, which can be readily detached from the rest of the system for inspection and adjustment. In this connection, the collector electrode is pulled tightly against the supporting yokes and ambers, after which the whole face of the assembly is first machined, and then ground and polished as a single unit—thus assuring accurate coplanarity of the faces. This construction also facilitates the accurate measurement of the collector width and air gaps, since the unit can be easily placed upon the table of a micrometer microscope.

[7] For description, see page 772 BS J. Research 9 (1932), RP505.

VII. TEMPERATURE OF CHAMBER

Temperature correction for a standard X-rayionization chamber is roughly ⅓ percent per degree centigrade. Heat dissipation inside the guarded-field chamber by the potential divider when operating at 2,100 volts is slightly less than 1 watt. To be certain that this did not influence the air temperature within a sealed chamber, simultaneous temperature measurements were made at the center and the outside of the chamber over a long period of time. A maximum difference of about 0.2° C was noted.

VIII. CURRENT COMPENSATION

Attention is called to another source of error which may be encountered in using any of the standard null methods of current measurements. It is of the "personal-error" type caused by failing to maintain the collector system sufficiently near ground potential during the balancing process. We have found, depending upon the operator and the voltage sensitivity of the electrometer, that a given operator tends to over-balance or under-balance consistently during the exposure time. This usually can be avoided by increasing the voltage sensitivity to the point just below which operation becomes troublesome from electrical and mechanical instability. For example, in one standard tested, a consistent potential difference of 0.2 volt between guard and collector electrode was found to introduce an error of 2 percent in the current measurement. This is, of course, an extreme effect since, with experience, one tends to balance out the deviations.

WASHINGTON, November 6, 1935.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP866

Part of Journal of Research of the National Bureau of Standards, Volume 16, February 1936

MESLE'S CHORD METHOD FOR MEASURING THE THICKNESS OF METAL COATINGS

By William Blum and Abner Brenner

ABSTRACT

This study was made to improve methods for measuring the thickness of an electroplated coating at any specified part of the surface. The "chord" method depends upon just cutting through the coating on a plane surface, with a grinding wheel of known radius, or on a curved surface, with a fine file. In either case the thickness T can be computed from C, the width of the cut, that is, the chord, and R, the radius of the wheel or curved surface, by the equation

$$T=\frac{C^2}{8R}.$$

Tests on coatings of known thickness showed that the results are accurate within about 10 percent for coatings at least 0.0002 in. (0.005 mm) thick. This accuracy compares favorably with the results obtained by measuring metallographic cross sections, a method that is more laborious and time-consuming than the chord method.

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I. INTRODUCTION

Specifications for electroplated coatings that were recently adopted by the American Society for Testing Materials and the American Electroplaters' Society include requirements for the minimum, rather than the average, thickness of the deposits. The successful application of such specifications demands simple, reliable methods for measuring the thickness of the coating at any given part of the article. Recently published dropping tests[1] are valuable for zinc and cadmium coatings. For deposits of nickel, copper, silver, and chromium, microscopic measurements of cross sections are usually employed. These require considerable time of skilled operators.

In a recent article by F. C. Mesle[2] entitled Standard Quality for Plated Tableware, there was described an ingenious method for

[1] R. O. Hull and P. W. C. Strausser, Monthly Rev. Am. Electroplaters' Soc. 22 (March 1935).
[2] Metal Ind. (N. Y.) 33, 283 (1935).

measuring the thickness of deposits. He urged "further study and refinement for greater convenience and accuracy." The purpose of this paper is to explain more fully the principles and calculations involved, and to describe typical procedures for applying this method to miscellaneous articles and coatings. As the results obtained indicate that under favorable conditions an accuracy of about 10 percent is usually obtainable, the method warrants thorough trial to determine whether it should be incorporated into formal specifications.

II. PRINCIPLES AND CALCULATIONS

The principle of the method is illustrated in figure 1. If a grinding wheel of radius R just cuts through a plated coating of thickness T

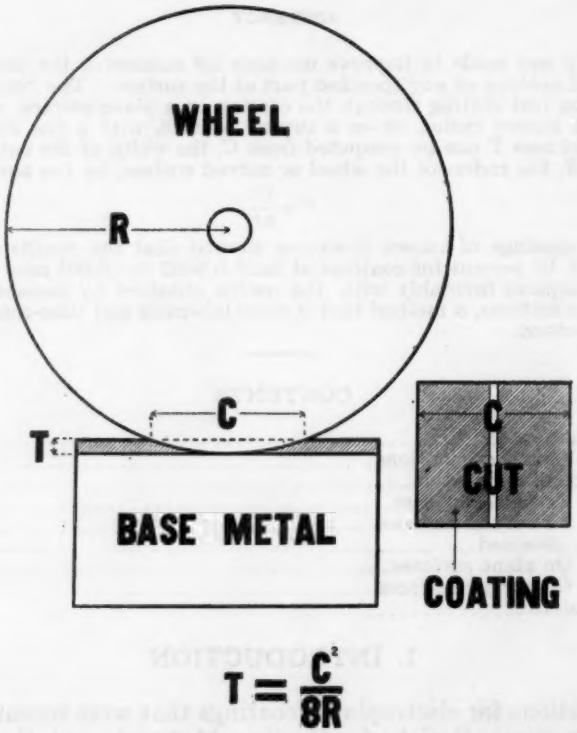

FIGURE 1.—*Testing a coating on a plane surface with a grinding wheel.*

on a flat surface, the width C of the cut is determined by the thickness, which can therefore be computed from R and C. Exactly the same relations exist if, as in figure 2, the coating on a curved surface of radius R is just cut through with a flat file. In either case the only dimensions required to calculate the thickness T (which is equal to the "sagitta" of the arc) are R, the radius of the wheel or plated surface, and C, the "chord", that is, the width of the cut.

Simple geometric calculations show that for both cases (figs. 1 and 2) the following equation must be used to calculate the thickness very accurately:

$$T=R-\tfrac{1}{2}\sqrt{4R^2-C^2}. \tag{1}$$

Suppose the radius of a plated tube is 2 in., and the width of the cut produced with a file is 0.2 in., that is, $R=2$ and $C=0.2$. Then

$$T=2-\tfrac{1}{2}\sqrt{4\times 2^2-(0.2)^2}=0.002\ 501\ 6 \text{ in.}$$

Calculations by eq 1 are very laborious, since seven-place logarithms must be used to obtain fair accuracy in the fourth decimal place. Fortunately the calculation can be much simplified for those cases in

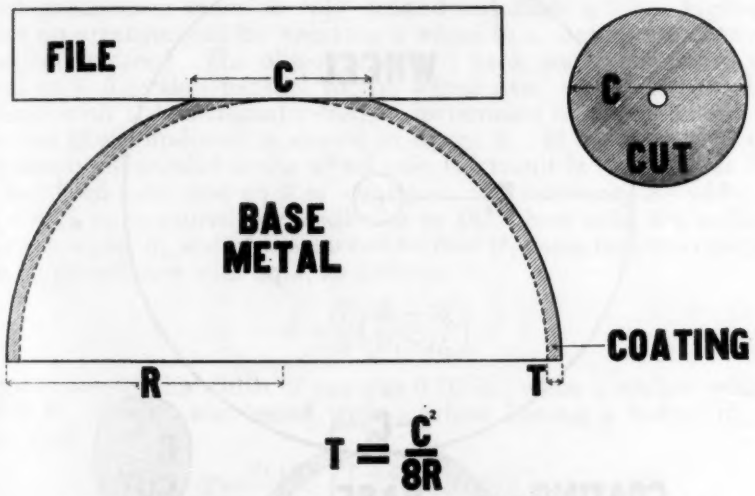

FIGURE 2.—*Testing a coating on a spherical surface with a file.*

which the thickness is small compared to the radius, which cases include almost all plated coatings (except on wires). The above exact equation can be expanded into a series, of which only the first term is necessary for moderate accuracy under the conditions specified. The simplified equation is

$$T=\frac{C^2}{8R}. \tag{2}$$

If the above problem is solved by this equation, we have

$$T=\frac{(0.2)^2}{8\times 2}=0.0025 \text{ in.},$$

which differs by less than one part in 1,000 from the exact value. For the number of significant figures usually justified, this result is identical with the value computed from the more exact equation.

It is evident that this is a mechanical method of magnifying the thickness, in contrast to the optical methods, which employ a microscope. In the example cited, the effective magnification is

$$\frac{0.2}{0.0025}=80.$$

From eq 2 it may be shown that the degree of magnification, that is, $\frac{C}{T}$, is equal to $\sqrt{\frac{8R}{T}}$. Therefore, the magnification for a given thickness is

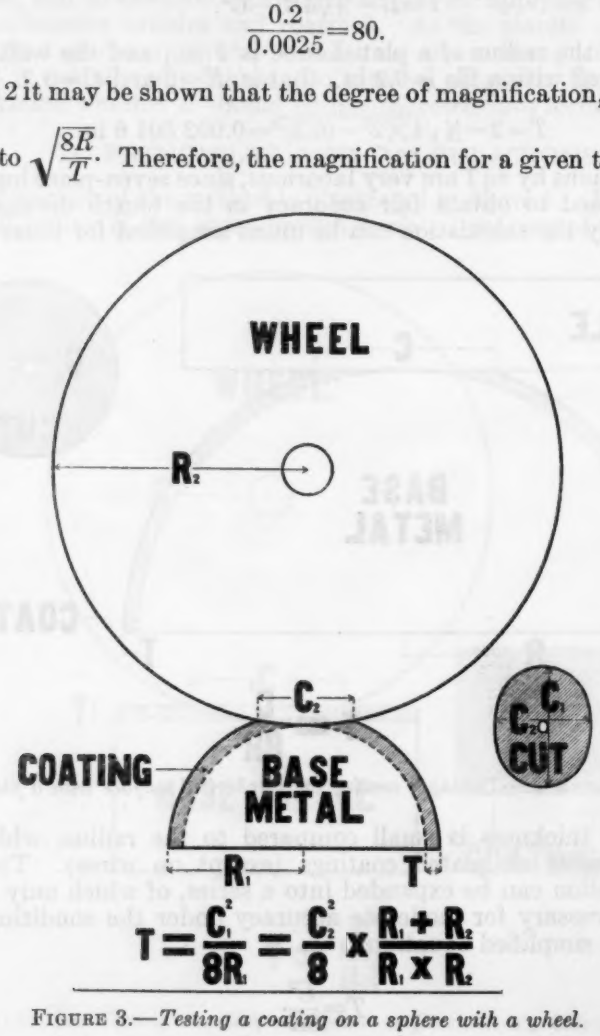

FIGURE 3.—*Testing a coating on a sphere with a wheel.*

increased (but not proportionally) by enlarging the diameter of the wheel; and for a given size of wheel the magnification increases as the thickness of coating decreases. In testing flat surfaces, the grinding wheel should therefore be the largest that will run very true on the machine used. On curved surfaces the effective magnification for a given thickness is fixed by the radius of curvature.

Equation 2 indicates the precision in the thickness measurement that will result from a given precision in measuring C and R. As the thickness varies as C^2, any error in measuring C will produce about twice that relative error in the calculated thickness. For practical measurements, where an accuracy of $\pm$ 10 percent is usually desired,

the width should therefore be measured with a precision of at least 5 percent. With the average pocket lens and scale, it is possible to measure a width as small as 0.08 in. (2.0 mm) with this precision on the average plated surface. This width of cut is produced by a wheel with a radius of 4 in. on a coating 0.0002 in. thick. The method is therefore not accurate with much thinner coatings, on which, moreover, the definition of the narrower cuts is less distinct.

Equation 2 shows that an error in measuring the radius of the wheel or plated surface produces about the same percentage error in the calculated thickness. The small changes in the radius of the wheel that occur during its moderate use are therefore not significant, but the wheel should be measured often enough to know its radius within about 2 percent.

When a curved surface has a radius of more than 1 in., a grinding wheel produces a more sharply defined cut than a file. Figure 3 shows an arrangement for applying a wheel to a coating on a convex spherical surface.[3] The object is moved back and forth under the wheel in a direction parallel to the wheel axis, while the wheel is lowered with the micrometer-feed in increments of about 0.0002 in. The cut thus produced is shown in figure 3. If the width of cut C_1 is measured parallel to the wheel axis, the result is the same as if a file had been used, and eq 2 is employed. If, however, the width of the cut C_2 is measured perpendicular to the wheel axis, the radii of both the wheel R_2 and of the curved surface R_1 enter into the calculation, in accordance with eq 3, as follows:

$$T=\frac{C_2^2}{8}\left(\frac{R_1+R_2}{R_1\times R_2}\right). \tag{3}$$

If, for example, the width of cut was 0.10 in., when a surface with a radius R_1, of 1 in. was tested with a wheel having a radius R_2, of 4 in., then

$$T=\frac{(0.10)^2}{8}\left(\frac{1+4}{1\times 4}\right)=0.0016 \text{ in.}$$

For testing a cylinder, the arrangement shown in figure 4 may be used, with the axis of the wheel perpendicular to the axis of the cylinder. The cut is made in the way described for figure 3, and has the section shown in figure 4. If the width is measured in direction C_1, the result is the same as with a file, and eq 2 is used, with R_1, that is, the radius of the cylinder. If the cut is measured in direction C_2, the result is the same as if the wheel had cut a plane surface. Equation 2 is again used, but with R_2, that is, the radius of the grinding wheel.

One objection that might be raised to the chord method is that it is necessary to expose an appreciable area of the base metal to detect it with certainty. This difficulty is entirely eliminated if, as is recommended, the width is measured at the point where the base metal is just exposed. Practically, however, the error made by disregarding a

[3] It is possible to apply the chord method to a coating on a *concave* surface by cutting into it with a grinding wheel with a radius *smaller* than that of the curved surface. The equation then becomes

$$T=\frac{C^2}{8}\left(\frac{R_1-R_2}{R_1\times R_2}\right).$$

As this method is difficult to apply in practice, and as the thickness on concave surfaces is not usually important no actual measurements were made to test this method.

very small width of exposed base metal is usually negligible. Suppose, for example, that in making a flat circular cut on a sphere (fig. 2) the width C_2 of the exposed base metal is 10 percent of the width C_1 of the entire cut. The true thickness may then be computed from eq 4, as follows:

$$T=\frac{C_1^2}{8R}-\frac{C_2^2}{8R}. \tag{4}$$

If C_2 is only 10 percent of C_1, C_2^2 is only 1 percent of C_1^2; that is, an error of only 1 percent is made by disregarding an exposed width of 10 per-

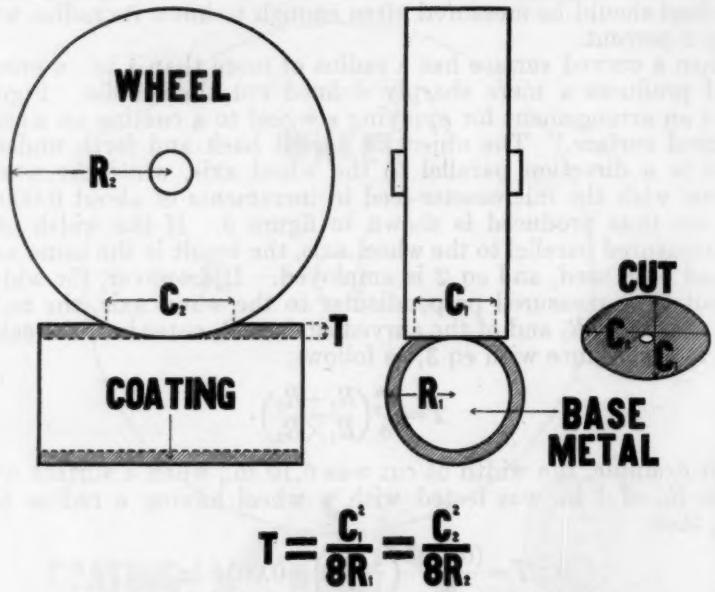

FIGURE 4.—*Testing a coating on a cylinder with a wheel.*

cent. It should be noted that it is not permissible merely to subtract C_2 from C_1, which would be equivalent to using the following *incorrect* eq 5:

$$T=\frac{(C_1-C_2)^2}{8R}, \tag{5}$$

which, in the above example, would produce an error of about 20 percent.

III. METHODS OF APPLICATION

1. TO PLANE SURFACES

For testing the coatings on nearly flat surfaces, a precision surface grinder with a magnetic chuck is convenient. A 6- or 8-inch grinding wheel, (R=3 or 4 in.), with a face 0.15 to 0.5 in. wide, is usually satisfactory. The wheel radius should be measured within about 2 percent. The wheel must revolve rapidly, about 3,000 rpm, which for an 8-inch wheel, corresponds to a peripheral speed of about 6,000 ft/min. The surface of the wheel should be dressed at intervals with a diamond to keep it cylindrical. Precise feed of the wheel is necessary to make sharp cuts. It is essential that the specimen be held very

rigidly. Steel pieces can usually be held directly on the magnetic chuck. Nonferrous metals may sometimes be held on this chuck with steel strips, otherwise mechanical clamps must be used.

If the wheel is brought down so that it just cuts the plane surface, and the latter is moved parallel to the wheel axis, a cut with parallel edges (fig. 5 (A)) will be produced.[4] If this cut does not expose the base metal, the wheel is lowered slightly, for example 0.0002 in., and a deeper cut is made, and so on until the base metal is just exposed (fig. 5 (B)). The width C of the last cut is then measured.

There are two practical difficulties in applying this procedure. It involves making repeated cuts, and it is difficult to just expose the base metal. Moreover, most commercially flat surfaces are not

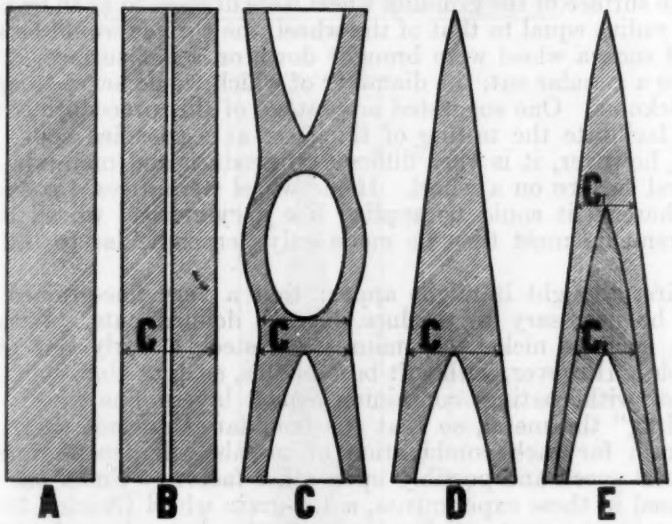

FIGURE 5.—*Appearance of typical cuts with a wheel on a flat surface.*

A. Parallel cut that has not exposed the base metal.
B. Parallel cut with slight exposure of base metal.
C. Cut produced on a surface that is not quite plane, exposing base metal at invervals. The thickness T can be computed from the chord with C, wherever the base is just exposed.
D. Tapered cut produced by slightly inclining the plate.
E. Tapered cut on plate with a composite coating. The thickness of each coating may be computed from the chord width where the next lower layer is just exposed.

exactly plane, and in practice the cut is likely to resemble figure 5 (C), on which the base metal is exposed for only part of the length. This behavior suggested a simple modification that is useful on more nearly flat surfaces. The surface is tilted slightly, for example, by putting a sheet of paper under one edge of the magnetic chuck. The cut (fig. 5 (D)) then tapers, and it is easy to note where the base metal is just exposed, and to measure the width C at that point. The thickness is then calculated by eq 2. With multiple coatings (fig. 5 (E) and 6) the thickness of each layer is computed from the

[4] By careful use of the micrometer-feed on the surface grinder, the thickness of the coating can be measured directly, but usually with a precision of not greater than 0.0002 in. As this represents an error of 20 percent in coatings 0.001 in. thick, the method is not reliable for any thinner coatings. To make such a direct measurement, the gage on the micrometer-feed is read when the wheel touches the surface of the coating and again when the coating is just cut through. The difference is the thickness of the coating.

width of cut (C_1 or C_2), where the next lower layer is just exposed. If the surface, for example, on cast plates, is wavy and a cut like figure 5 (C) is produced, it is unnecessary to tilt the plate, as the width C can be measured wherever the base metal is just exposed.

If a perfectly flat plate be slightly tilted so as to produce a cut like figure (D) it is possible to calculate the thickness from the *length* of the cut up to the point where the base metal is just exposed, provided that the angle of tilt is known exactly. This method can be used to yield a very high magnification, and has been occasionally employed in the examination of coatings. Actually, however, the surface is never exactly plane, and it is practically impossible to measure with even moderate accuracy a very small angle, such as one with a tangent of 0.001.

If the surface of the grinding wheel were dressed so as to be convex, with a radius equal to that of the wheel, the surface would be spherical. If such a wheel were brought down on a flat surface, it would produce a circular cut, the diameter of which would serve to measure the thickness. One suggested advantage of this procedure is that it would facilitate the testing of thickness at a specified spot. Practically, however, it is very difficult to produce and maintain a true spherical surface on a wheel. If the wheel were dressed convex but not spherical, it could be applied like a cylindrical wheel, but the measurements must then be made only perpendicular to the wheel axis.

At first thought it might appear that a very fine-grained wheel would be necessary to produce sharply defined cuts. With hard metals, such as nickel, chromium, and steel, a fairly fine grain is desirable. However, with soft base metals, such as zinc, copper, and brass, or with coatings containing copper layers, fine wheels fill up and "drag" the metal, so that the boundaries are not sharp. The best grain for each combination of metals will depend upon the peripheral speed and possibly upon other factors. Under the conditions used in these experiments, a 120-grain wheel (Norton 38120 J) was found to be most satisfactory for the hard metals, and a 90-grain (Norton 3890 H) for soft base metals.

No high magnification is required or warranted for measuring the widths of the cuts, as, with high enlargement, the edges are very irregular. A pocket lens with a magnification of about 12 diameters, and a thin steel scale graduated to 0.01 in., are usually adequate for a precision of 5 percent. The combination of lens and metric scale (fig. 7) that is commonly used for measuring Brinell hardness indentations is very convenient.

2. TO CURVED SURFACES

In the method described and used by Mesle for testing the thickness of silver on a spoon, the latter was rubbed on a fine, flat file until the base metal was just exposed. The curvature of the surface at the point tested was determined with a multiple template, and the width of cut was measured with a transparent scale, after which the thickness was calculated as above.

Tests made at this Bureau on spheres and cylinders have shown that the cuts made with a fine file (for example no. 6) are very satisfactory if certain precautions are observed. It is essential that the

FIGURE 6.—*Cut produced on composite coating of nickel, copper, nickel on steel* (× 2).

Total thickness 0.002 inch. The dark center portion is the exposed steel that has been treated with copper sulphate to produce contrast. The next dark area is the copper layer between two nickel layers.

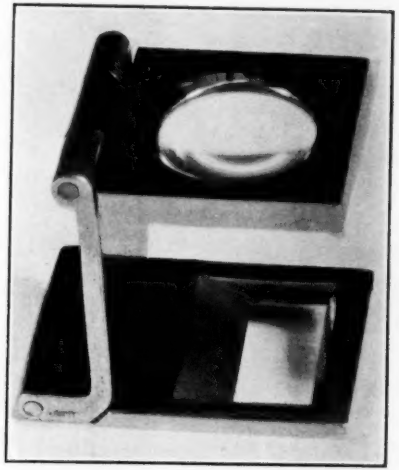

FIGURE 7.—*Pocket lens and scale (usually metric).*

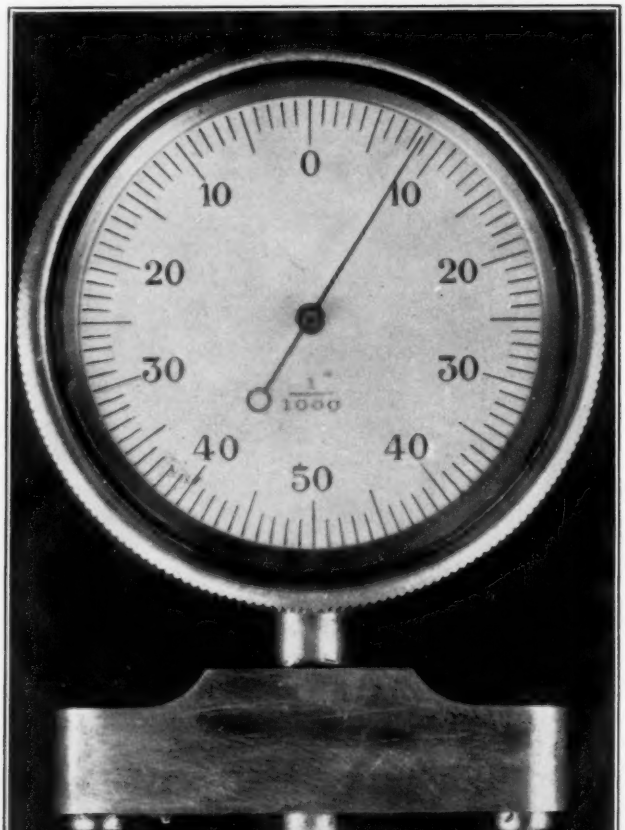

FIGURE 8.—*Typical spherometer for measuring curvatures of surfaces.*

file travel in a plane, that is, it must not "rock" longitudinally, and if measurements are to be made in two directions, it must not rock transversely. Rocking can be prevented by attaching, to the vise which holds the specimen, a steel support that is level with the surface to be tested and is a few inches away. The file rests on this support and the article and is thus kept in a plane. For routine testing of similar articles, a filing machine could probably be adapted to making the cuts.

The curvatures of spherical, cylindrical, or conical surfaces of small radii, for example up to 1.0 in., can be measured with fair accuracy with suitable templates, such as the sets of radius gages that are used in machine shops. Surfaces with larger radii can usually be measured with a "spherometer" [5] (fig. 8), the principle of which is similar to that involved in the chord method. Certain types of spherometer are regularly used for measuring curvatures of optical surfaces, such as spectacle lenses. It is possible to calibrate a spherometer to give a direct reading of the curvature. Otherwise, the radius can be computed from eq 6:

$$R=\frac{C^2}{8T}+\frac{T}{2}, \tag{6}$$

where R is the radius, C the chord, and T the sagitta of the arc measured.

At best it is very difficult to measure a curvature that is not constant over the length of arc covered by the spherometer or gage. In such cases the curvature may be approximated by assigning limits to it.

IV. RESULTS OBTAINED

1. ON PLANE SURFACES

The accuracy of the chord method was determined by comparing its results with the average thicknesses estimated from the total weights of deposit on pieces that were plated with precautions to insure nearly uniform distribution. These included some of the steel specimens prepared for the exposure tests that were conducted jointly by the American Electroplaters' Society, American Society for Testing Materials, and National Bureau of Standards,[6] and of the nonferrous metals now being prepared for new exposure tests. In fact, this method has recently been used as a regular means of testing the thickness and distribution of coatings on the nonferrous specimens. In a few cases the results were also checked by microscopic measurements on cross sections taken adjacent to the points where the chord method was applied.

In the accompanying tables, the term "Set" refers to the corresponding specimens in the exposure tests. Each result for the chord method represents the average of from 10 to 20 measurements on that

[5] It has been suggested that a spherometer or similar dial gage might be used to measure directly the thickness of the coating by noting the difference in reading before and after the coating is filed or ground through. The principle of this method is sound, but its precision is usually less than that of the chord method. This may be illustrated by a typical example. If the curvature of a sphere with a 1-in. radius is measured with a spherometer having the points 1 in. apart, the length of the sagitta (from which the radius is computed) is about 0.135 in., which can readily be measured to ± 2 percent. If the coating is 0.001 in. thick, the corresponding chord is 0.09 in., which can be measured with a lens and scale to ± 5 percent, corresponding to ± 10 percent in the computed thickness. If the latter is measured directly with a spherometer an appreciable error might arise from the difficulty of exactly replacing the points after the cut is made; and an error of 20 percent would be produced by an error of 0.0002 in. in reading the dial.

[6] W. Blum, P. W. C. Strausser, and A. Brenner, J. Research NBS 13, 331 (1934) RP712.

specimen. The "errors" reported in the tables are the deviations from the values based on the weights of the coatings. As the deposits were never absolutely uniform in thickness, errors of less than 5 percent are probably not significant.

When there was a difference in the color of the coating and the base metal, the line of demarcation was usually distinct. Even with zinc and cadmium on steel, exposure of the steel was easily detected. With nickel on steel it was found most satisfactory to treat the cut surface with a neutral, saturated solution of copper sulphate, which caused deposition of copper on the steel but not on the nickel. With deposits of nickel or chromium on brass or nickel-brass, better contrast was obtained by treating the surface with a solution containing chromic acid and sulphuric acid, or with a solution of ammonium persulphate, both of which etch the base metal.

Measurements by different observers showed that the precision of individual readings of width was usually about 0.004 in. (0.1 mm), that is, from 2 to 4 percent of the usual chord lengths of 0.10 to 0.20 in. (2.5 to 5 mm). This represents an error of 4 to 8 percent in the computed thickness. The average reading error of a number of measurements was considerably less.

With grinding wheels having radii of 3 to 4 in., it was impossible to make clearly marked cuts less than about 0.04 in. (1 mm) wide. This corresponds to a thickness of about 0.000 05 in. (0.001 25 mm), which is therefore the least thickness measurable under these conditions. Practically, the method possesses very little accuracy for coatings less than 0.0002 in. (0.005 mm). It therefore is not applicable to the very thin coatings of chromium (about 0.000 02 in. or 0.0005 mm) that are regularly used for decorative purposes. For such coatings a very small grinding wheel or stone might be used to produce a narrow but well-defined cut, the width of which could be measured with a microscope.

TABLE 1.—*Nickel and composite coatings on steel plates*

[Average thickness]

Experiment	Set	Coating measured	Weight thickness	Microscopic		Chord	
				Thickness	Error	Thickness	Error
			Inch	*Inch*	*Percent*	*Inch*	*Percent*
1	52	Ni	0.000 27			0.000 27	0
2	5	Ni	.000 52	0.000 50	−4	.000 53	+2
3	5	Ni	.000 50			.000 52	+4
4	101	Ni	.001 04			.001 05	+1
5	101	Ni	.001 04			.001 09	+5
6	6	Ni	.001 99			.001 99	0
7	111	Cu+Ni	.001 07			.001 07	0
		Cu	.000 54			.000 51	−6
		Ni	.000 53			.000 54	+2
8	17	Ni+Cu+Ni	.001 04			.001 01	−3
		Ni	.000 19			.000 16	−16
		Cu	.000 30			.000 25	−17
		Ni	.000 55			.000 59	+7
9	16	Ni+Cu+Ni	.001 96	.001 88	−4	.001 91	−3
		Ni	.000 39	.000 38	−3	.000 37	−5
		Cu	.000 58	.000 56	−4	.000 54	−7
		Ni	.000 99	.000 94	−5	.000 99	0
		Average error			−4		±5

Another factor in the accuracy is the smoothness of the coating and of the base metal. Almost all satisfactory commercial plating that has been buffed is sufficiently smooth to yield well-defined cuts. If, however, the base metal is rough, for example from excessive pickling or sandblasting before plating, the definition is poor and the results are unreliable.

The data in table 1 show that the average accuracy for nickel or composite coatings on steel is about ±5 percent, which compares favorably with the accepted metallographic methods. The only errors greater than 10 percent were for the relatively thin layers in composite coatings.

From the contrast between the colors of nickel and of copper or brass, it might be expected that the method would be especially adaptable to nickel coatings on these metals. Actually, however, as shown in table 2, the accuracy was not as high as on other base

TABLE 2.—*Nickel coatings on copper and brass plates*

[Average thickness]

Experiment	Set	Base metal	Weight thickness	Chord	
				Thickness	Error
			Inch	*Inch*	*Percent*
1	C 1	Copper	0.000 19	0.000 22	+16
2	C 1	do	.000 20	.000 19	−5
3	C 2	do	.000 49	.000 54	+10
4	C 2	do	.000 50	.000 50	0
5	B 32	Brass	.000 11	.000 15	+36
6	B 21	do	.000 26	.000 28	+8
7	B 38	do	.000 19	.000 22	+16
8	B 34	do	.000 49	.000 49	0
9	B 34	do	.000 58	.000 56	−4
10	N 5	Ni-brass	.000 21	.000 18	−14
				Average error	±11

metals. The cuts for the experiments in table 2 were made with a 90-grain wheel (Norton 3890H), and the exposed base metals were etched with a mixture of chromic and sulphuric acids. When a 120-grain wheel was used, the results were about 20 percent low. In spite of the fact that zinc-base die castings are softer than brass, the

TABLE 3.—*Nickel coatings on zinc-base die-cast plates*

[Average thickness]

Experiment	Weight thickness	Chord	
		Thickness	Error
	Inch	*Inch*	*Percent*
1	0.000 28	0.000 30	+7
2	.000 47	.000 49	+4
3	.000 89	.000 90	+1
		Average error	±4

results in table 3 for nickel coatings on such alloys were very satisfactory.

The results in tables 4 and 5 show that the method is applicable to coatings of soft metals such as zinc and cadmium on steel. The

TABLE 4.—*Zinc coatings on steel plates*

[Average thickness]

Experiment	Set	Weight thickness	Chord	
			Thickness	Error
		Inch	*Inch*	*Percent*
1	207	0.000 23	0.000 26	+13
2	208	.000 54	.000 56	+4
3	209	.001 07	.001 09	+2
4	215	.001 04	.001 12	+8
5	219	.000 87	.000 89	+2
		Average error		±6

TABLE 5.—*Cadmium coatings on steel plates*

[Average thickness]

Experiment	Set	Weight thickness	Chord	
			Thickness	Error
		Inch	*Inch*	*Percent*
1	310	0.000 19	0.000 20	+5
2	302	.000 55	.000 58	+5
3	312	.001 00	.001 03	+3
		Average error		±4

TABLE 6.—*Chromium coatings*

[Average thickness]

Experiment	Set	Base metal	Weight thickness	Chord	
				Thickness	Error
			Inch	*Inch*	*Percent*
1	128	Ni on steel	0.000 06	0.000 06	0
2	154	do	.000 11	.000 08	−27
3	B 24	Brass	.000 23	.000 21	−9
4	N 1	Nickel-brass	.000 22	.000 17	−23
			Average error		±15

accuracy shown in table 6 with a very hard metal (chromium), is fair, even though the coatings were relatively thin. For such thin coatings, microscopic examination is preferable.

2. ON CURVED SURFACES

The data in tables 7 and 8 show that the accuracy on curved articles is fully equal to that on plane surfaces. There was no consistent difference in the results obtained with a file and a wheel, although it was observed that on articles with a radius of 1 in. or more, the definition of the cut was sharper with a wheel than with a file.

The results of measurements in the two directions were very concordant, even though with cylinders the chord measured perpendicular to the wheel axis was much longer than the chord that was parallel to the wheel axis (fig. 4).

TABLE 7.—*Nickel coatings on brass cylinders*

[Average thickness]

Wheel axis perpendicular to cylinder axis:
⊥ indicates cut measured perpendicular to wheel axis.
= indicates cut measured parallel to wheel axis.

Experiment	Radius of cylinder	Method		Weight thickness	Chord	
		Device	Measure		Thickness	Error
	Inches			*Inch*	*Inch*	*Percent*
1	2.00	Wheel	⊥	0.000 62	0.000 69	+11
		do	=	.000 62	.000 66	+6
		File		.000 62	.000 72	+16
2	1.00	Wheel	⊥	.000 66	.000 68	−3
		do	=	.000 66	.000 68	−3
		File		.000 66	.000 68	−3
3	0.5	Wheel	⊥	.000 65	.000 58	−11
		do	=	.000 65	.000 56	−14
		File		.000 65	.000 58	−11
4	0.25	Wheel	⊥	.000 64	.000 68	+6
		do	=	.000 64	.000 64	0
		File		.000 64	.000 62	−3
					Average error	±8

TABLE 8.—*Zinc coatings on steel spheres*

[Average thickness]

⊥ indicates cut measured perpendicular to wheel axis.
= indicates cut measured parallel to wheel axis.

Experiment	Radius of sphere	Method		Weight thickness	Chord	
		Device	Measure		Thickness	Error
	Inch			*Inch*	*Inch*	*Percent*
1	1	Wheel	⊥	0.001 23	0.001 30	+6
		do	=	.001 23	.001 25	+2
		File		.001 23	.001 35	+9
2	0.5	Wheel	⊥	.001 53	.001 54	+1
		do	=	.001 53	.001 62	+6
		File		.001 53	.001 52	−1
3	0.25	Wheel	⊥	.001 94	.001 64	−15
		do	=	.001 94	.001 68	−13
		File		.001 94	.001 64	−15
4	0.25	File		.002 09	.002 20	+5
					Average error	±7

TABLE 9.—*Silver on the outside of teaspoons*

[Average thickness]

Experiment	Portion tested	Average radius of curvature	Micrometer thickness	Chord	
				Thickness	Error
		Inch	*Inch*	*Inch*	*Percent*
1	Not overlaid	0.70	0.000 95	0.000 78	−18
2	Overlay	.74	.003 6	.003 6	0
	Rest of bowl	.63	.001 34	.001 34	0
3	Overlay	.74	.003 8	.003 5	−8
	Rest of bowl	.67	.001 21	.001 23	+2
				Average error	±6

The results in table 9 were obtained on nickel-brass teaspoons that had been plated by F. C. Mesle with a separable silver deposit, so that the thickness of the coating adjacent to the file cut could be measured with a micrometer after removing the coating. The average accuracy of ± 6 percent is just about equal to that reported by Mesle for similar measurements. One difficulty with spoons is that the radius of curvature varies over the length of the bowl, and it is hard to measure this radius accurately at any given point.

V. CONCLUSIONS

1. The chord method can be applied by cutting through a coating on a plane surface with a grinding wheel of known radius, or on a curved surface with a file or grinding wheel.

2. The thickness of the coating can be computed from the equation

$$T=\frac{C^2}{8R},$$

where T is the thickness, C is the chord, that is, the width of the cut where the base metal is just exposed, and R is the radius of the grinding wheel, or of the curvature of the surface tested.

3. The method is simple and quick, and the results usually agree within about 10 percent with microscopic measurements and with the average thickness computed from the weight of coating. For coatings less than 0.0002 in. (0.005 mm) the method is not very accurate, and the microscopic method is preferable.

4. Although the coating is necessarily damaged in the test, the base metal is penetrated so little that the tested articles can usually be salvaged by stripping, polishing, and replating.

The authors desire to express their appreciation to F. C. Mesle, of the Oneida Community, and to P. W. C. Strausser and C. Kasper, of this Bureau, for assistance and suggestions during this investigation.

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CORROSION-PROTECTIVE VALUE OF ELECTRODEPOSITED ZINC AND CADMIUM COATINGS ON STEEL

By William Blum, Paul W. C. Strausser,[1] and Abner Brenner

ABSTRACT

Atmospheric exposure of plated specimens in six locations showed that in a rural or purely marine climate, both zinc and cadmium coatings furnished better protection against the corrosion of steel than did nickel or chromium coatings of the same thickness, although the zinc and cadmium rapidly lost their luster. In an industrial atmosphere, where sulphurous and sulphuric acids are present, both zinc and cadmium were attacked rather rapidly, and the life was about proportional to the thickness. Under these conditions the cadmium coatings failed in about two-thirds of the time required for failure of zinc coatings of the same thickness. Zinc-cadmium alloys containing about 10 percent of cadmium were superior to either zinc or cadmium. Variations in the conditions selected for depositing the coatings did not have a marked effect on their protective value. Hot-dipped zinc coatings gave about the same protection as plated zinc coatings *of the same thickness.*

In accelerated tests, such as the salt spray or intermittent immersion in a solution of sodium chloride, the time required for failure of a zinc coating is about proportional to its thickness. Cadmium coatings last much longer than those of zinc in a salt spray, which is not, therefore, a true measure of their relative value in an industrial atmosphere.

The protective value of a zinc or cadmium coating depends principally upon its minimum thickness, which can be determined by dropping tests, microscopic measurements, and the chord method.

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I. INTRODUCTION

During the past few years, exposure tests and accelerated tests of electroplated steel have been conducted through cooperation of the American Electroplaters' Society and the American Society for Testing Materials with the National Bureau of Standards. The results obtained with nickel and chromium finishes have been published [1], [2].[2] The purpose of this paper is to describe and discuss the results obtained in about 3.5 years' atmospheric exposure of zinc and cadmium coatings, and of a few deposits consisting of alloys of zinc and cadmium. As conclusive results have thus far been obtained only in severe industrial locations, this report is subject to revision in the light of longer exposures in marine or rural locations. However, as the specifications for commercial coatings are determined largely by the most severe conditions that are likely to be encountered, it is improbable that the results of longer exposures will materially change the practical application of the data. Accelerated tests and measurements of thickness were also made on these deposits.

Many of the procedures in this investigation were identical with those used for the nickel and chromium finishes. Full details of such operations are contained in Research Papers RP712 and RP724 [1], [2].

II. PREPARATION OF SPECIMENS

1. BASE METAL

The base metal was cold-rolled strip steel SAE 1010, of the same lot that was used for the nickel and chromium finishes. It had a good finish and received no polishing prior to plating. Each specimen was 4 by 6 in. (10 by 15 cm).

[2] The numbers in brackets here and throughout the text refer to the references at the end of this paper.

2. PREPARATION FOR PLATING

In general, the methods used in cleaning and pickling the steel were the same as those used previously in nickel and chromium plating, though a few minor variations were applied. In both the cleaning and plating processes, a certain convenient procedure was arbitrarily selected as a "standard." This designation does not imply that it was superior, but merely shows that it served as a basis of comparison.

The procedures may be summarized as follows:

Standard cleaning "A."

"1." Most of the grease was removed with carbon tetrachloride. The plates were then:

"2." Cleaned cathodically in a hot solution containing sodium carbonate (30 g/liter or 4 oz/gal), trisodium phosphate (30 g/liter or 4 oz/gal), and sodium hydroxide (7.5 g/liter or 1 oz/gal);

"3." Scrubbed with a bristle brush;

"4." Rinsed in hot water;

"5." Pickled in warm dilute sulphuric acid (98 g/liter or 13 oz/gal);

"6." Rinsed in cold water.

Cleaning followed by hydrogen expulsion "A–1."

The procedure was exactly as in "A", except that after step "6", the plates were hung for 5 minutes in the hot cleaning solution without current; and were again scrubbed and rinsed. This procedure was found most effective to overcome blistering of zinc coatings produced in cyanide solutions, although it was also used for some of the acid-zinc deposits. Without this treatment, many of the zinc plated specimens developed large blisters on standing or on heating to 110° C. No such blisters were observed on specimens subjected to this "hydrogen expulsion." It is believed that the final heating in alkali eliminated much of the hydrogen absorbed during the pickling operation. This could no doubt have been accomplished by heating in boiling water, but the alkaline solution prevented the tarnishing that might have occurred in water. No reason can be given for the fact that, without this step, equally good adherence was obtained with some of the acid-zinc coatings and some of the cadmium coatings.

Cathode pickling "B."

The procedure was the same as in "A", except that instead of the direct pickling in step "5", cathode pickling was used.

Anode pickling "C."

The procedure was the same as in "A", except that after step "5" the steel was pickled anodically in 96 percent sulphuric acid, and was quickly rinsed in cold water.

3. CONDITIONS USED IN PLATING

Twelve specimens were plated simultaneously. Although the deposits were somewhat thicker near the edges than in the center, subsequent tests by the dropping method [3] showed that on at least 80 percent of the area the thickness varied less than 10 percent from that specified. The chemicals and anodes used in the plating were analyzed and found to be of good commercial quality. The solutions

were analyzed at intervals and were adjusted to within about 2 percent of their nominal compositions.

(a) ZINC PLATING

Cast-zinc anodes were used. The conditions of operation are summarized in table 1. Although the addition of mercuric oxide to the solution used in method "O" corresponds to about 1 percent as much mercury as zinc, some of the deposits were found to contain over 2 percent of mercury, which is somewhat higher than is commonly recommended.

The pH of the acid-zinc solutions was measured with a quinhydrone electrode. In the acid baths the zinc anodes were surrounded with muslin bags to prevent roughness of the deposits, and the cathodes were shaken occasionally to detach bubbles and thus prevent pitting.

TABLE 1.—*Conditions in zinc plating*

A. CYANIDE SOLUTIONS

Method	Composition of solution					Temperature		Current density		Variation [1]
	$Zn(CN)_2$	NaCN	NaOH	HgO	pH	°C	°F	amp/dm²	amp/dm²	
N (*N*)	1.0	0.5	1.3			22	70	2	19	Standard.
N (g/liter)	60	23	53							
N (oz/gal)	8	3	7							
O (*N*)	1.0	.5	1.3	0.0016		22	70	2	19	Mercury.
O (g/liter)	60	23	53	.35						
O (oz/gal)	8	3	7	.05						

B. ACID SOLUTIONS

Method	$ZnSO_4 \cdot 7H_2O$	Na_2SO_4	$AlCl_3 \cdot 6H_2O$	Dextrin	pH	Temperature		Current density		Variation
P (*N*)	3	1	0.25		3.5	35	95	5	47	High sulphate.
P (g/liter)	410	75	20							
P (oz/gal)	54	10	3							
Q (*N*)	3		.25		3.5	22	70	3	28	Dextrin.
Q (g/liter)	410		20	7.5						
Q (oz/gal)	54		3	1						

[1] In this and succeeding tables, the term "variation" refers to the essential difference from the "standard" procedure.

(b) CADMIUM PLATING

Cast-cadmium anodes were used. The conditions of operation are summarized in table 2. Solution "S" contained "gulac", a waste product of the sulphite-pulp industry, which was selected as a typical organic addition agent. Solution "T" contained gulac and also a very small amount of nickel sulphate, an inorganic addition agent. The deposits from the plain solution "R" were dull and coarsely crystalline; those from "S" were smooth and fairly bright; and those from "T" contained about 0.015 percent of nickel and were still brighter.

TABLE 2.—*Conditions in cadmium plating*

Method		Composition of solution					Temperature		Current density		Variation
		CdO	NaCN	NaOH	Gulac[1]	$NiSO_4.7H_2O$	°C.	°F.	amp/dm²	amp/dm²	
R	*N*	0.35	1.5	0.4			22	70	1	9	Standard
	g/liter	23	75	15							
	oz/gal	3	10	2							
S	*N*	.7	2.5				22	70	2	19	Gulac.
	g/liter	45	120		12						
	oz/gal	6	16		1.6						
T	*N*	.7	2.5			0.007	22	70	2	19	Gulac+ nickel.
	g/liter	45	120		12	1					
	oz/gal	6	16		1.6	0.13					

[1] A waste product of the sulphite-pulp industry.

(c) DEPOSITION OF ZINC-CADMIUM ALLOYS

Deposits containing about 10 percent of cadmium and 90 percent of zinc were readily obtained by using anodes of that composition in bath "U", described in table 3. It was difficult to produce consistently deposits with 5 percent of cadmium, as planned. Even when the content of cadmium in the bath was greatly reduced, the deposits contained about 8 percent of cadmium. Coatings containing about 15 percent of cadmium (14 percent by actual analysis) were obtained by increasing the content of cadmium in the bath. Efforts to control the cadmium content by regulating the current density were not very successful, though in general the cadmium content was decreased by increasing the current density.

TABLE 3.—*Conditions for depositing zinc-cadmium alloys*

Method		Composition of solution				Temperature		Current density		Variation
		$(CN)_2Zn$	CdO	NaCN	NaOH	°C.	°F.	amp/dm²	amp/ft.²	
U	*N*	1.2	0.05	0.75	2.25	35	95	2	19	10% of cadmium.
	g/liter	75	3	38	90					
	oz/gal	10	.4	5	12					
U-1	*N*	1.2	.015	.75	2.25	35	95	2	19	8% of cadmium.
	g/liter	75	1	38	90					
	oz/gal	10	.13	5	12					
U-2	*N*	1.2	.10	.75	2.25	35	95	2	19	14% of cadmium.
	g/liter	75	6.5	38	90					
	oz/gal	10	.9	5	12					

4. SCHEDULE OF DEPOSITS[3]

The conditions used and the thickness of each deposit are summarized in tables 4, 5, and 6. None of the deposits were buffed. The corresponding total weights of the coatings on both sides of the sheet, expressed in oz/ft² of sheet metal, have been computed in table 4 for zinc coatings in order to facilitate their comparison with the hot-dipped coatings (such as set 219), for which the thickness on sheet metal is usually so expressed.

[3] Most of the experimental work was conducted with metric measurements. However, as the thickness of the coatings was specified in fractions of an inch, the English units of thickness have been used in this paper, in some cases with metric equivalents. The conversions are in all cases approximate, as no high precision was involved.

TABLE 4.—*Preparation of zinc coatings*

Set	Cleaning method	Plating			Variation
		Method	Thickness	Weight [1]	
			Inch	Oz/ft²	
201	A–1	N	0.0005	0.59	Cyanide:
202	B, A–1	N	.0005	.59	Cathode pickle.
203	C	N	.0005	.59	Anode pickle.
205	A–1	N	.0002	.24	Thickness.
206	A–1	N	.0010	1.18	Thickness.
207	A–1	O	.0002	.24	Cyanide + mercury:
208	A–1	O	.0005	.59	Thickness.
209	A–1	O	.0010	1.18	Thickness.
210	A	P	.0005	.59	Acid, high sulphate:
214	A	P	.0002	.24	Thickness.
215	A	P	.0010	1.18	Thickness.
216	A–1	Q	.0002	.24	Acid dextrin:
217	A–1	Q	.0005	.59	Thickness.
218	A–1	Q	.0010	1.18	Thickness.
219		Hot galvanized	.0009	1.05	Hot dipped.

[1] The total weight of coating on both sides of the sheet.

TABLE 5.—*Preparation of cadmium coatings*

Set	Cleaning	Plating		Variation
		Method	Thickness	
			Inch	
301	A	R	0.0005	Standard:
302	B	R	.0005	Cathode pickle.
303	C	R	.0005	Anode pickle.
304	A	R	.0002	Thickness.
305	A	R	.0010	Thickness.
307	A–1	S	.0002	Gulac brightener:
308	A–1	S	.0005	Thickness.
309	A–1	S	.0010	Thickness.
310	A–1	T	.0002	Gulac + nickel:
311	A–1	T	.0005	Thickness.
312	A–1	T	.0010	Thickness.

TABLE 6.—*Preparation of zinc-cadmium alloy coatings*

Set	Cleaning	Plating		Variation
		Method	Thickness	
			Inch	
401	A	U	0.0005	10% of cadmium:
402	A	U	.0002	Thickness.
403	A	U	.0010	Thickness.
404	A	U–1	.0005	8% of cadmium.
405	A	U–2	.0005	14% of cadmium.

III. ATMOSPHERIC-EXPOSURE TESTS

1. CONDITIONS OF EXPOSURE

Five specimens of each set were exposed in the spring of 1932 in each of six locations, namely Key West (K.W.), Fla.; New York City (N.Y.), N. Y.; Pittsburgh (P.), Pa.; Sandy Hook (S. H.), N. J.; State College (S. C.), Pa.; and Washington (W), D. C. The specimens were supported on galvanized steel racks by means of porcelain insulators. They were inclined 30 degrees from horizontal and faced south.

2. INSPECTION

At specified intervals, at first of a few weeks and later of a few months, the specimens were examined by members of the joint inspection committee and other interested persons. The average number of persons at each inspection was three.

The approximate proportion of the surface rusted was expressed by the scale of ratings shown in table 7. As the specimens had not

TABLE 7.—*System used for rating of specimens*

Surface rusted		Rating	Corresponding score	Surface rusted		Rating	Corresponding score
Range	Average			Range	Average		
	Percent		*Percent*		*Percent*		*Percent*
0 percent		5	100	10 to 20 percent	15	2	40
0 to 5 percent	2.5	4	80	20 to 50 percent	35	1	20
5 to 10 percent	7.5	3	60	50 to 100 percent	75	0	0

(a) METHOD OF RATING

been buffed, the entire surface of each plate was included in the inspections. (In the inspections of nickel and chromium finishes, rust near the edges was disregarded, because the thickness of the coatings there had been reduced by buffing.) The cut edges of the hot-dipped specimens (set 219) were protected with a black paint. Each inspector assigned a numerical rating on the above scale to each specimen, and the average of the ratings of all the inspectors for a set of specimens constituted the recorded "rating" (R) for that set, location, and inspection date. The mean of this and the rating at the preceding inspection, that is, the average rating for the period, was multiplied by the number of weeks intervening to obtain the "score" (S) for the period. The total score for the entire period of the tests was compared with a perfect score for the same period to obtain the "percentage" score (T%). If, for example, the ratings for a set at the end of 20 and 24 weeks were 4 and 3, respectively, the average rating for that period was 3.5, and the score was $3.5 \times 4 = 14$. If the total score for the 20 weeks previously elapsed was 76, the score for the entire 24 weeks was $76 + 14 = 90$, instead of the possible perfect score of $24 \times 5 = 120$, and the percentage score was $90/120 = 75$ percent.

The net result was to express the quality on a percentage basis, which, however, as shown in table 7, is not proportional to the per-

centage of unrusted surface. It is possible, however, to approximately convert the scores to percentages of rust in order to compare the results with those of other investigations. This can be conveniently done by use of figure 1, based on the average percentage

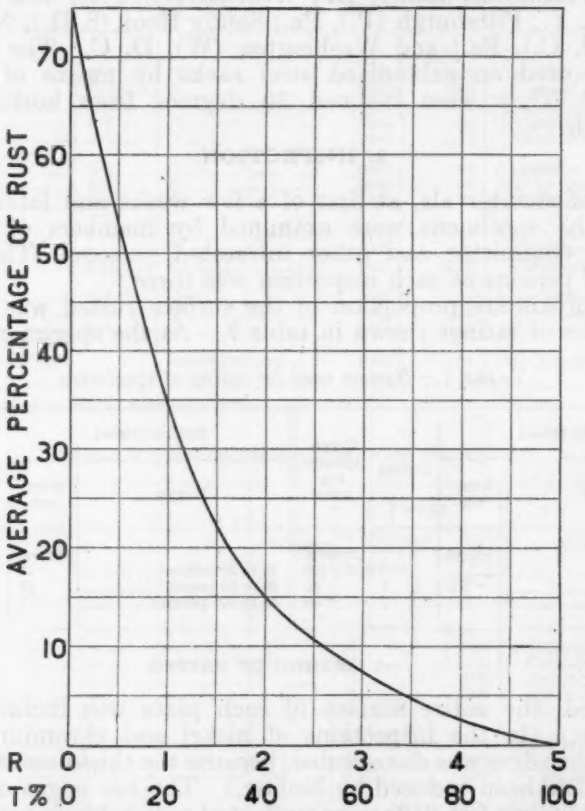

FIGURE 1.—*Relation between rating* (R), *percentage score* (T%) *and average percent of rust.*

of rust for each rating. (This conversion has been made in fig. 4.) The use of this roughly logarithmic scale is justified by the fact that for many purposes a small amount of rust is relatively more significant than a large amount. Another advantage is that a difference, for example of 10 percent, in the percentage score corresponds approximately to the same proportional difference in the extent of rust, whether this is small or large.

(b) APPEARANCE

As zinc and cadmium coatings are generally used outdoors only when appearance is at most a secondary factor, no effort was made to rate other defects on the specimens, such as loss of luster, or the presence of stains or white coatings. Incidental observations were made, however, that will be referred to later.

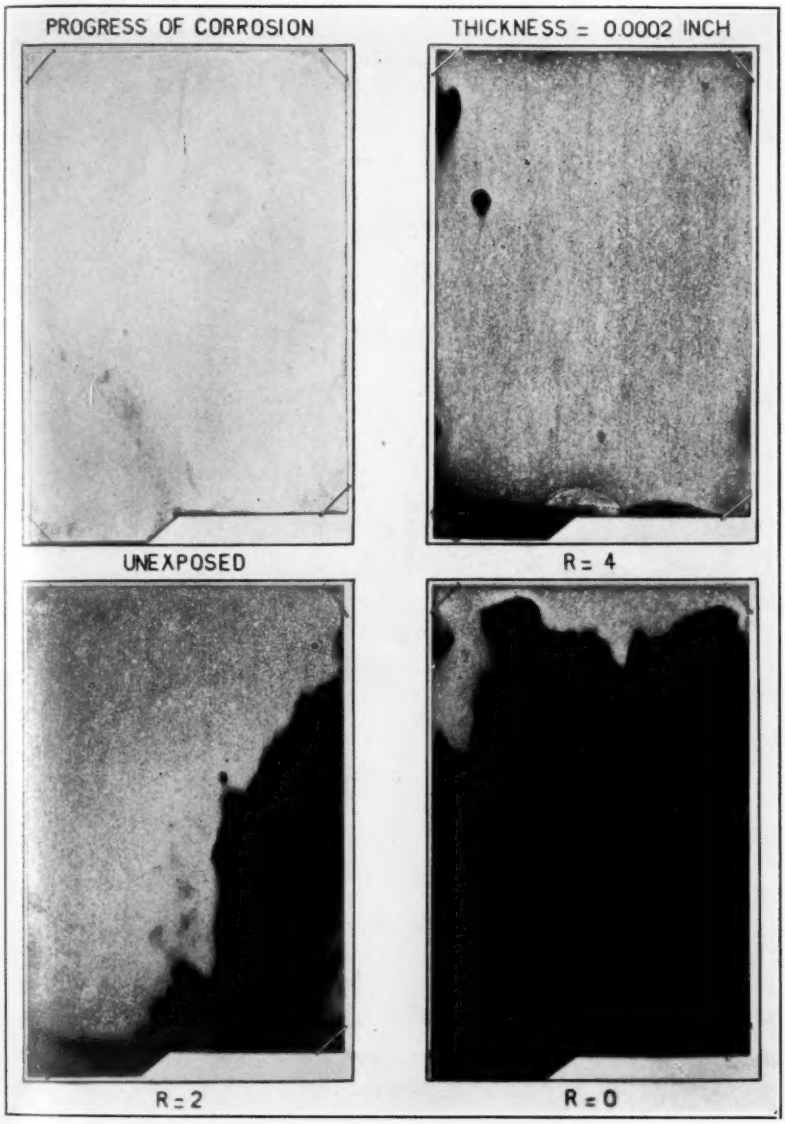

FIGURE 2.—*Progress of corrosion of steel coated with 0.0002 inch of zinc at Washington after 180 weeks' (3.5 years) exposure.*

None of these specimens showed appreciable corrosion at the end of 160 weeks. The dark areas represent red rust. Cadmium coated specimens behaved similarly.

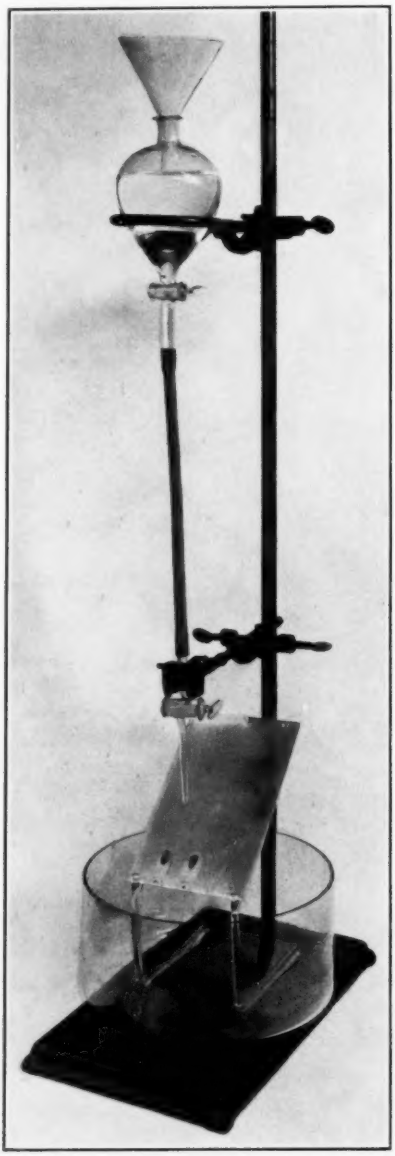

FIGURE 8.—*Apparatus used in dropping tests for thickness of zinc and cadmium coatings.*

3. SIGNIFICANCE OF EXPOSURE TESTS

In the report on nickel and chromium coatings it was pointed out that in actual service on automobiles, the finishes are usually washed at intervals and are often waxed, whereby their protective value may be increased. Consequently the results of continuous exposure tests without cleaning do not necessarily represent the behavior of such coatings in service. However, as zinc and cadmium coatings are rarely washed or waxed when used outdoors, the results of the exposure tests probably represent closely the behavior of such finishes in actual service in comparable atmospheres.

4. RESULTS OF EXPOSURE TESTS

The behavior and present status of all the sets are summarized in table 8.

(a) REPRODUCIBILITY

The data for the zinc and cadmium coatings show that, especially in industrial locations, there was even closer agreement in the reports of several inspectors than with the nickel and chromium finishes previously reported. This agreement was caused by the fact that although the latter more noble coatings usually fail by permitting rusting in pin holes, the coatings of less noble metals such as zinc and cadmium generally furnish complete protection of the steel until the coating is entirely dissolved from a relatively large part of the area, which then rusts. In almost every case the rusting started along the lower edge, where moisture adhered longest, and then spread up the sides and finally to the center, figure 2. This figure shows that the rate of solution of the zinc varied on different parts of the same specimen, which explains the failure of these relatively uniform coatings to dissolve simultaneously from the entire surface of each specimen. It is easier to estimate the proportional area of one or of a few large rust spots than of a large number of very small spots.

In the marine atmosphere at Key West, almost all the zinc- and cadmium-coated specimens (regardless of thickness), developed in one to two years a few very small rust spots, which did not materially increase in number or size during more prolonged exposure. This amount of rust, corresponding to a rating of 4, apparently does not represent an appreciable destruction or weakening of the base metal, which is very evident when failure occurs in an industrial climate. It is difficult to reconcile the presence of these small rust spots with the well-known tendency of zinc and cadmium to protect small exposed areas of steel against corrosion, especially as the adherent film of salt water is conducting. An explanation may be found in the fact that in a marine atmosphere the zinc and cadmium become coated with insoluble films, which may insulate the metal coatings, and thus prevent them from exercising their "sacrificial" effect on the adjacent small exposed areas of steel. If this explanation is correct, freedom from pores is more important in zinc and cadmium coatings that are exposed to a marine climate than in those exposed to industrial conditions, even though the pores may not result in structural damage.

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TABLE 8.—*Summary of exposure tests to November 1, 1935 (about 180 weeks' exposure)*

ZINC

Set	Description	Thickness	Key West [1]	New York					Pittsburgh					Sandy Hook					State College				Washington					Set
				R [2]	Rust	T	Weeks to R=		R	Rust	T	Weeks to R=		R	Rust	T	Weeks to R=		R	Rust	T	Weeks [4] to R=	R	Rust	T	Weeks to R=		
			T [3]				3	0				3	0				3	0				3				3	0	
		Inch	%		%	%				%	%				%	%				%	%			%	%			
201	Cyanide	0.0005	93	0	75	53	93	143	0	75	55	118	162	5	0	98	-----	-----	5	0	100	-----	5	0	100	-----	-----	201
202	Cathode pickle	.0005	98	0	75	41	83	93	0	75	54	118	132	4.6	1	99	-----	-----	5	0	100	-----	4.9	1	100	-----	-----	202
203	Anode pickle	.0005	96	0	75	43	93	100	0	75	51	118	118	4	3	97	-----	-----	5	0	100	-----	4.9	1	100	-----	-----	203
205	Cyanide	.0002	94	0	75	28	52	65	0	75	29	55	81	0	75	53	100	143	5	0	100	-----	2	3	96	-----	-----	205
206	do	.0010	92	0.4	55	74	143	175	1.2	28	91	173	-----	5	0	98	-----	-----	5	0	100	-----	5	0	100	-----	-----	206
207	Cyanide+Hg	.0002	90	0	75	30	57	75	0	75	22	45	55	0	75	55	108	121	5	0	100	-----	0.3	60	89	173	188	207
208	do	.0005	93	0	75	60	121	143	0	75	63	132	162	5	0	99	-----	-----	5	0	100	-----	4.9	1	100	-----	-----	208
209	do	.0010	88	4	3	93	181	-----	0.4	56	88	173	-----	5	0	99	-----	-----	5	0	100	-----	4.9	1	100	-----	-----	209
210	Acid+SO_4	.0005	86	0	75	49	100	108	0	75	52	118	118	5	0	98	-----	-----	5	0	100	-----	4.6	1	100	-----	-----	210
214	do	.0002	85	0	75	27	52	57	0	75	23	50	50	0	75	50	93	108	5	0	100	-----	0	75	78	148	173	214
215	do	.0010	89	0	75	83	169	169	4.0	3	91	-----	-----	5	0	98	-----	-----	5	0	100	-----	4.5	1	98	-----	-----	215
216	Acid+dextrin	.0002	89	0	75	28	52	57	0	75	24	50	60	0	75	59	108	121	5	0	100	-----	0	75	81	159	188	216
217	do	.0005	87	0	75	52	100	108	0	75	55	118	118	4.8	1	97	-----	-----	5	0	100	-----	4.7	1	100	-----	-----	217
218	do	.0010	86	0.6	48	83	169	169	3.6	4	93	-----	-----	5	0	99	-----	-----	5	0	100	-----	4.8	1	99	-----	-----	218
219	Hot dip	.0009	85	0	75	76	121	169	0	75	86	173	183	4	3	98	-----	-----	4.8	1	100	-----	4.8	1	100	-----	-----	219

CADMIUM

CADMIUM

301	Cyanide	0.0005	81	0	75	26	57	65	0	75	43	98	118	4	3	94			5	0	100		4	3	97			301
302	Cathode pickle	.0005	81	0	75	25	57	65	0	75	42	89	118	3.4	5	94			5	0	100		4.3	2	97			302
303	Anode pickle	.0005	81	0	75	25	52	65	0	75	41	81	118	3.8	4	95			5	0	100		3.8	4	94			303
304	Cyanide	.0002	81	0	75	16	33	40	0	75	17	36	50	0	75	43	93	108	3.6	4	94		0	75	59	112	148	304
305	do	.0010	81	0	75	44	93	121	0.2	65	81	162	183	5	0	94			4.8	1	100		4.3	2	96			305
307	Gulac	.0002	81	0	75	16	33	40	0	75	17	36	42	0	75	47	100	121	3	8	85	178	0	75	58	112	148	307
308	do	.0005	81	0	75	27	57	65	0	75	37	81	118	4	3	88			5	0	100		4.3	2	97			308
309	do	.0010	81	0	75	46	100	121	0	75	71	132	173	5	0	96			5	0	100		5	0	100			309
310	Gulac+Ni	.0002	81	0	75	14	33	40	0	75	18	36	45	0	75	46	83	108	3	8	87	159	0	75	78	126	159	310
311	do	.0005	82	0	75	28	57	75	0	75	34	60	98	3.2	6	90			5	0	100		4.4	2	96			311
312	do	.0010	82	0	75	44	93	108	0	75	81	162	183	5	0	97			5	0	100		4.8	1	99			312

ZINC—CADMIUM ALLOY

401	10% of cadmium	0.0005	87	0	75	58	108	143	0	75	69	132	162	5	0	98			5	0	100		4.8	1	99			401
402	do	.0002	86	0	75	28	57	57	0	75	25	50	60	0	75	53	100	108	5	0	100		0	75	76	148	159	402
403	do	.0010	85	4	3	94			5	0	97			5	0	99			5	0	100		4.9	1	99			403
404	8% of cadmium	.0005	89	0	75	62	121	143	0	75	60	118	162	5	0	99			5	0	100		4.9	1	99			404
405	14% of cadmium	.0005	87	0	75	60	121	143	0	75	58	118	162	5	0	98			5	0	100		5	0	100			405

[1] All sets at Key West have a rating of 4, corresponding to 3 percent of rust.
[2] T=total score, in percent.
[3] R=Rating.
[4] No sets at State College have reached a rating of 0.

(b) EFFECT OF LOCATION

The prevailing atmosphere has a very marked effect upon the rate of failure of zinc and cadmium coatings. The behavior of thin coatings (0.0002 in.) is illustrated in figure 3. This shows complete failure of both zinc and cadmium in industrial locations (New York and Pittsburgh) in about a year; in Sandy Hook, a combined marine and industrial atmosphere, in about 2 years; and in Washington, a mild urban location, in about 3 years. On the other hand, neither metal showed decided failure in 3 years in either a marine location (Key West) or a rural exposure (State College). As thick coatings have failed severely only at New York and Pittsburgh, detailed comparisons of the coatings must be confined to these two locations.

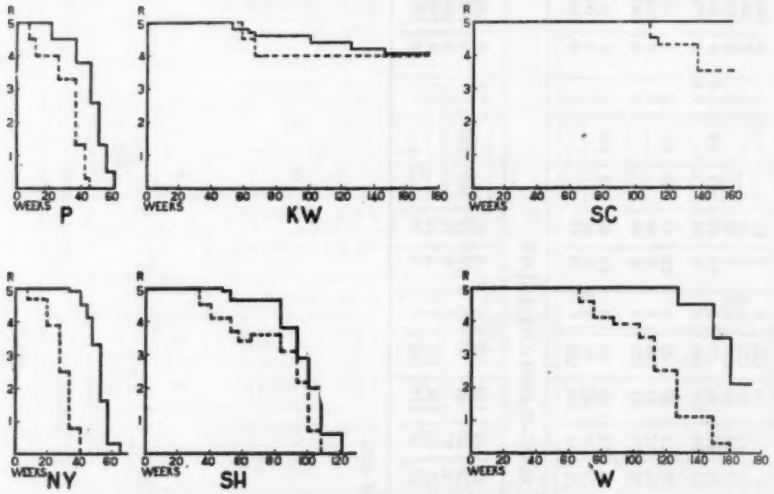

FIGURE 3.—*Rates of corrosion of steel plated with 0.0002 in. of zinc or cadmium, expressed as ratings R.*

The data represent the averages of four sets (20 specimens) of zinc and three sets (15 specimens) of cadmium in each location. P=Pittsburgh; KW=Key West; SC=State College; NY=New York; SH=Sandy Hook; W=Washington. Zinc ——— Cadmium - - - -

The more rapid failure of zinc and cadmium in industrial locations is undoubtedly caused by the higher concentrations of sulphur dioxide (and possibly of sulphur trioxide) in the atmosphere of such places. These sulphur compounds produce soluble salts of zinc and cadmium, which are readily removed by rain, the amount of which is therefore a secondary factor in the corrosion. That the rainfall is not a primary factor, as suggested by H. Figour and P. Jacquet [4], is evident from the very slow failure of these coatings at Key West, where the rainfall is relatively high.

In the absence of sulphur dioxide, it is probable that both metals are protected by thin films of basic carbonate. These are sometimes visible, expecially on zinc coatings in a marine atmosphere. Sulphur acids dissolve these films, and hence permit more rapid solution of the coating.

(c) COMPARISON OF ZINC AND CADMIUM

The data in figure 3 show conclusively that in industrial locations cadmium coatings fail more rapidly than do zinc coatings of equal thickness. As the specific gravity of cadmium (8.6) is about 20 percent greater than that of zinc (7.1), the comparison would be still less favorable to cadmium if coatings of equal weight per unit area were considered. These results fully confirm the conclusions of other investigators, based on loss of weight of zinc and cadmium coatings in New York [5], [6], in London [8], and in Paris [4].

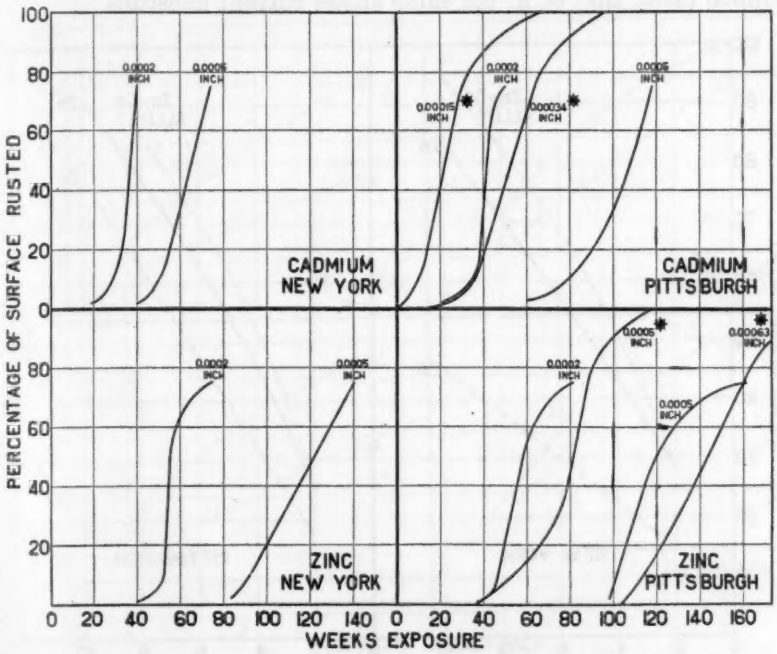

FIGURE 4.—*Average rates of corrosion of steel plated with different thicknesses of zinc or cadmium, expressed as percentage of surface rusted.*

Curves marked * are from figure 1 of the paper by Passano [reference 7], whose curve for 0.0005 in. of zinc is for a sherardized zinc coating, and for 0.00063 in. is for hot-dipped sheets.

The same conclusion may be reached from figure 4, in which the data for New York and Pittsburgh have been plotted in terms of the percentage of surface rusted, in order to make these results directly comparable with those of the ASTM tests on hardware [7]. (A few curves for coated hardware from the ASTM tests in Pittsburgh are included for comparison.) As indicated in figure 1 total failure (a rating of 0) may represent from 50 to 100 percent of rust, and has therefore been plotted as 75 percent. That complete failure of the plated flat specimens is more sharply defined than of the hardware specimens is caused partly by this method of rating, and partly by the fact that the latter are of irregular shape and hence the coatings are less uniform in thickness. It is evident, however, that the periods required for the major part of the rusting are consistent for coatings of similar thickness.

Consideration of the atomic weights of zinc and cadmium shows that electrochemically equivalent corrosion of the two metals would dissolve 1.72 times (by weight) as much cadmium as zinc. Hence, at any specified current density a given *weight* of cadmium would dissolve in 58 percent of the time required for the same weight of zinc. As, however, the specific gravity of cadmium is greater than that of zinc, it requires 71 percent as many ampere hours to dissolve the same *thickness* of cadmium as of zinc. As this ratio is about the same as that observed with the two metals in an industrial atmosphere, it is apparent that they are corroding at about the same electrochemical rates, that is, at the same anode current densities.

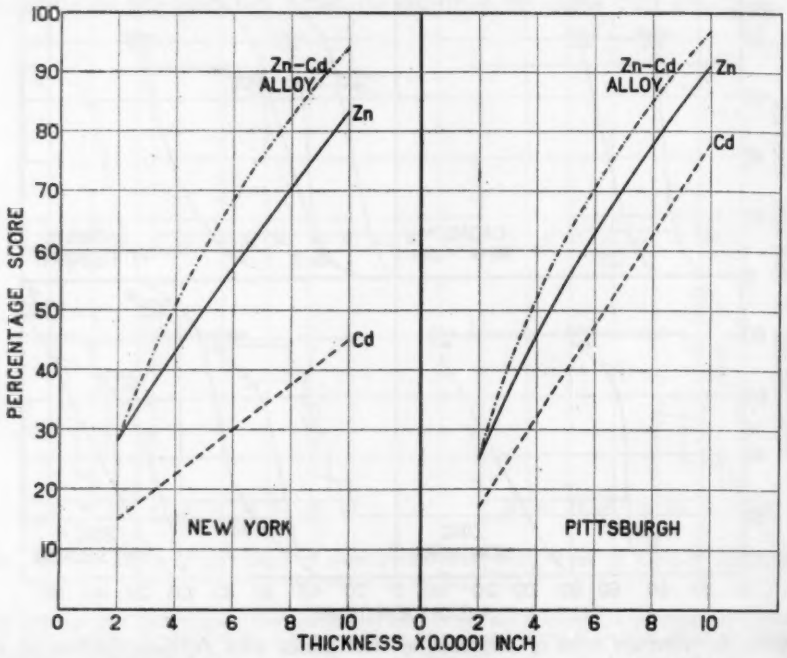

FIGURE 5.—*Relation between thickness of zinc, cadmium, or zinc-cadmium alloy, and percentage scores in New York and Pittsburgh, after 3.5 years' exposure.*

In mild locations, such as State College and Washington, thin coatings of both zinc and cadmium lasted a few years, but coatings of cadmium failed somewhat sooner than those of zinc. In marine locations the difference is not very significant. At Key West, the two coatings are in practically identical condition after 3 years, with only the few small rust spots referred to previously. It is evident that thin coatings of either of these metals furnish good protection for at least a few years against rural or marine exposures.

The curves in figure 5 show that deposits 0.0005 and 0.001 in. thick, that contain about 10 percent of cadmium and 90 percent of zinc, furnish somewhat better protection in industrial regions than do zinc coatings of the same thickness, although the scores for thinner coatings are practically identical. Similarly, Hippensteel and Borgman [6] found that alloy deposits containing 5 percent of cadmium corroded less rapidly than pure zinc deposits from cyanide baths.

(d) EFFECT OF THICKNESS

If, as is generally agreed, zinc and cadmium protect steel against corrosion by "sacrificial" action, their protective value should be proportional to their thickness, as has been frequently reported. [5], [6], [7], [9]. The curves of figure 5 show that, when expressed in terms of the percentage score, the protective value of either zinc or cadmium is practically a linear function of its thickness.

With zinc-cadmium alloys, the protective value does not increase quite linearly with the thickness, although the departure is not great. The same behavior is illustrated in figure 6, where are shown the

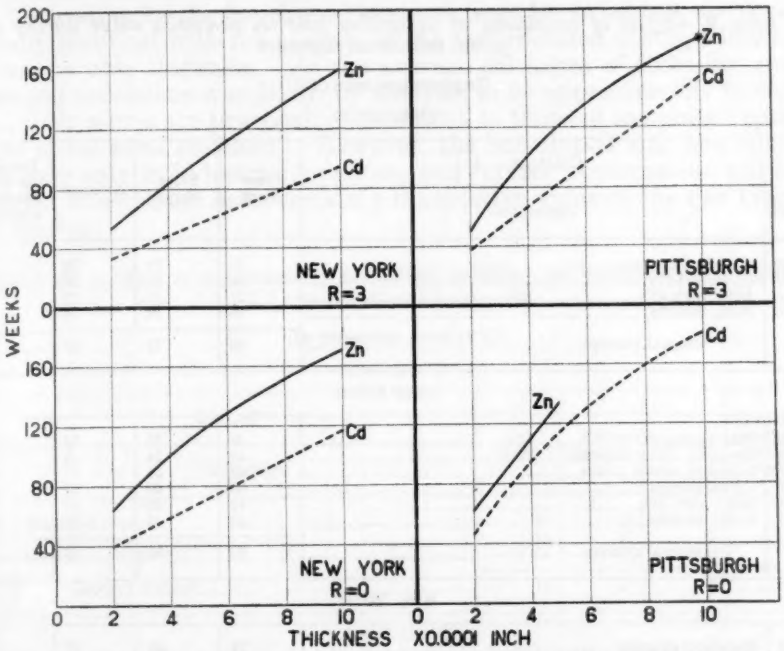

FIGURE 6.—*Time required on zinc and cadmium coated steel for first decided failure* (R=*3, i.e., (5 to 10 percent of rust), and for complete failure* (R=0, *i.e., over 50 percent of rust*).

The curve marked * is a minimum value as only two of the four sets have reached a rating of 3.

periods required to reach (a) a rating of 3, that is, from 5 to 10 percent of rust, and (b) a rating of 0, that is, over 50 percent of rust. While the data for failure of thick coatings in Pittsburgh are incomplete, the available results are consistent with those for New York. For practical purposes we may consider that the life of a zinc or a cadmium coating in an industrial atmosphere is proportional to its thickness. No evidence was found in these tests in support of the "critical thickness" mentioned by W. S. Patterson [8] for zinc coatings and by S. Wernick [9] for cadmium coatings. These authors found that in accelerated tests very thin coatings of these metals dissolved relatively much more rapidly than thicker deposits; and designated the point of inflection in the thickness-corrosion rate curve as a "critical thickness." In most of their experiments this was found to be about

0.0002 in. of either zinc or cadmium. They attributed the more rapid attack of thin coatings to their porosity. As the minimum thickness used in this investigation (0.0002 in.) was about equal to the reported critical thickness, no evidence was afforded as to the behavior of thinner coatings, or as to the existence of a critical thickness.

(e) EFFECT OF CONDITIONS OF DEPOSITION

(1) *Zinc.*—The data in table 9 show that the method of preparing this particular steel (such as anodic or cathodic pickling) had no marked effect upon the protective value of the coatings in industrial

TABLE 9.—*Effect of conditions of depositing zinc on protective value during 3.5 years' industrial exposure*

[In percentage score (T%)]

Coatings		New York	Pittsburgh	Average	Deviation from general average
Set	Description				
	0.0002 INCH				
205	Standard cyanide	28	29	29	+2
207	Cyanide+Hg	30	22	26	−1
214	Acid, high SO_4	27	23	25	−2
216	Acid, dextrin	28	24	26	−1
	General average	28	25	27	
	0.0005 INCH				
201	Standard cyanide	53	55	54	+1
202	Cyanide, cathode pickle	41	54	48	−5
203	Cyanide, anode pickle	43	51	47	−6
208	Cyanide+Hg	60	63	62	+9
210	Acid, high SO_4	49	52	51	−2
217	Acid, dextrin	52	55	54	+1
	General average	50	55	53	
	0.001 INCH				
206	Standard cyanide	74	91	82	−5
209	Cyanide+Hg	93	88	91	+4
215	Acid, high SO_4	83	91	87	0
218	Acid, dextrin	83	93	88	+1
	General average	83	91	87	
219	Hot dipped	76	86	81	−6

locations. There was no consistent difference in the behavior of deposits from cyanide and acid-zinc baths, though Hippensteel and Borgman [6] reported that zinc deposited from acid baths corroded more rapidly than that from cyanide baths. Observations, not included in the table, showed that the zinc deposits from cyanide solutions darkened more rapidly in the atmosphere than did those from acid baths, which was also reported by Hippensteel and Borgman. The common belief that better protection is obtained with zinc deposits from cyanide than from acid baths, is no doubt based partly on the fact that the throwing power of the cyanide solutions is superior to that of acid solutions, and that the coatings from cyanide baths are more uniformly distributed on irregularly shaped articles,

which therefore have a longer life. The results of this study simply show that if a given minimum thickness of zinc can be applied to an article there is no great difference in protective value, whether this is accomplished from a cyanide or an acid bath.

The presence of a small amount of mercury in the zinc coatings appears advantageous, as it produced an improvement of 9 percent in the score of set 208 (0.0005 in.). It remains to be seen whether thicker coatings (set 209) will show a similar relative improvement on longer exposure. Attention should be called to the fact that such deposits may not be desirable in contact with brass or aluminum, the corrosion of which is accelerated by mercury.

The results for the hot-dipped coatings (set 219) in table 9, are practically identical with the average of the electroplated coatings having a comparable thickness. As the average thickness of these hot galvanized specimens was found by analysis to be approximately 0.0009 in., their scores are practically equivalent to those of the plated coatings of *the same thickness*. However, the hot-dipped zinc has failed severely only in industrial locations, and further observations will be needed to establish more certainly the relative value of the two types of coating.

TABLE 10.—*Effect of conditions of depositing cadmium on protective value during 3.5 years' industrial exposure*

[In percentage score (T%)]

Coating		New York	Pittsburgh	Average	Deviation from general average
Set	Description				
0.0002 INCH					
304	Standard cyanide	16	17	17	0
307	Cyanide+gulac	16	17	17	0
310	Cyanide+gulac+Ni	14	18	16	−1
	General average	15	17	17	
0.0005 INCH					
301	Standard cyanide	26	43	35	+2
302	Cyanide, cathode pickle	25	42	34	+1
303	Cyanide, anode pickle	25	41	33	0
308	Cyanide+gulac	27	37	32	−1
311	Cyanide+gulac+Ni	28	34	31	−2
	General average	26	39	33	
0.001 INCH					
305	Standard cyanide	44	81	63	+1
309	Cyanide+gulac	46	71	59	−3
312	Cyanide+gulac+Ni	44	81	63	+1
	General average	45	78	62	

(2) *Cadmium.*—The data in table 10 show that the differences in the protective value of cadmium coatings produced under various conditions or from different cyanide baths are very small. As there was a marked difference in the initial appearance and probably in

the crystal structure of the three types of cadmium deposits, these results show that no advantage in protective value is *necessarily* obtained by making the deposits brighter or finer-grained. The use of a specific addition agent must therefore be justified by a demonstrated increase in protective value, by an improvement in the initial appearance of the coating or in the throwing power, or by some operating advantage. After a moderate period in a severe industrial location all the cadmium deposits turned dull and had about the same appearance. In a marine atmosphere the cadmium coatings had less white film and preserved a better appearance than did the zinc coatings.

(3). *Zinc-Cadmium Alloys.*—From a practical standpoint, it is important to know whether a small variation in the cadmium content of the alloy deposits has an appreciable effect on their behavior. It was found difficult to control closely the cadmium content of these deposits on flat plates, and it is reasonably certain that on irregularly shaped articles, where the current density is less uniform, the composition as well as the thickness may vary considerably. The results in table 11 show that moderate variations in the cadmium content, for example from 8 to 15 percent, have no significant effect on the protective value.

TABLE 11.—*Effect of composition of zinc-cadmium alloys on protective value during 3.5 years' industrial exposure*

[In percentage score (T%)]

0.0005-INCH COATING

Coating		New York	Pittsburgh	Average	Deviation from general average
Set	Cadmium content				
	Percent				
401	10	58	69	64	+3
404	8	62	60	61	0
405	14	60	58	59	−2
General average		60	62	61	

IV. ACCELERATED TESTS

In the accelerated tests that have been most frequently used to evaluate zinc and cadmium coatings, sodium chloride is the principal corroding agent. It might be predicted and has been approximately confirmed, that the results of such tests are at least similar to those in a marine atmosphere. In view of the fact, however, that both zinc and cadmium coatings fail much more rapidly in an industrial than in a marine location, it would be more logical to apply, in accelerated tests, the substances that are most significant in an industrial atmosphere, that is sulphurous and sulphuric acid. Although numerous efforts [10], [11], [12], [13] have been made to develop tests in which sulphurous acid is used, such tests have never been standardized or extensively applied. Unsuccessful efforts were made in this investigation to develop a sulphur dioxide test that can be conveniently operated and that will yield reproducible and significant results. There is a need for more study of such tests, especially for zinc and cadmium coatings.

In the salt spray and intermittent immersion tests the temperature was maintained at 35 ± 2° C (95 ± 4° F) in order to obtain reproducible results. This temperature was selected because it is about the lowest that can be maintained in the United States throughout the year without artificial cooling. The rate of the failure at this temperature is somewhat more rapid than at the lower temperatures that usually prevail in laboratories, but it is not feasible to fix any exact ratio of the results at different temperatures.

Before applying an accelerated test, the surface of each specimen was rubbed with a thin paste of very finely divided magnesium oxide and was rinsed. This produced a clean surface that was free from "water-break", that is, remained uniformly wet, which is a condition essential for reproducible results.

1. METHODS EMPLOYED

(a) SALT SPRAY

The salt-spray test was conducted with a 20-percent solution of pure, neutral, sodium chloride in a room kept at 35° C (95° F). The nozzle, air pressure and baffle were so adjusted as to keep a uniform fine mist throughout the box and to wet uniformly the specimens, which were supported on glass at an angle of 45° from horizontal. The solution that was condensed from the spray was drained off and not used again.

The specimens were inspected at the end of the first 6 hours and of each succeeding 24-hour period. (The elapsed intervals have been rounded off to multiples of 5 for convenience of reference.) At each inspection, the specimens were washed with running water and allowed to dry, because then the amount of rust could be more accurately estimated than when they were wet. With some coatings, especially zinc deposits that had been in the salt spray or intermittent immersion for a considerable period, the white coating (probably basic zinc carbonate) was so adherent that light scrubbing with a bristle brush was required to remove it. It was found that such specimens failed somewhat sooner than unscrubbed specimens. Complete removal of the white coating evidently permitted more rapid subsequent corrosion of the zinc.

Just as in the exposure tests, the zinc- and cadmium-coated specimens tended to corrode in relatively large areas, instead of in the fine rust spots that usually appear on nickel and chromium finishes. As a consequence, it was easier to estimate the extent of the corroded area and to assign a rating from 5 to 0, on the same basis as in the atmospheric-exposure tests.

(b) INTERMITTENT IMMERSION

The intermittent immersion tests were also conducted with a 20-percent solution of sodium chloride. Each cycle included 1 minute in the solution and 14 minutes in the air. The temperature was kept at 35° C (95° F) and the relative humidity at 60 ± 5 percent. Under these conditions the specimens were visibly wet for about one-half of each period in the air. The specimens were inspected at the same intervals as those in the salt spray and the condition of each was similarly recorded.

TABLE 12.—*Accelerated tests on zinc and cadmium coatings*

A. ZINC—0.0002 INCH

Coating		Atmospheric average score NY+P	Salt spray			Intermittent immersion		
			Initial rust		Rating 100 hours R	Initial rust		Rating 100 hours R
Set	Description		To R=4	To R=0		To R=4	To R=0	
		Percent	hr	hr		hr	hr	
205	Standard cyanide	29	80	120	1.3	25	50	0
207	Cyanide+Hg	26	80	120	1.3	25	55	0
214	Acid, high SO_4	25	60	110	.3	25	55	0
216	Acid, dextrin	26	60	110	1.0	25	55	0
	Average	27	70	115	1.0	25	55	0
	0.0005 INCH							
201	Standard cyanide	54	140	410	4.0	60	120	1.0
202	Cyanide, cath. pickle	48	110	390	4.5	70	140	2.0
203	Cyanide, anode pickle	47	120	240	3.5	60	100	1.0
208	Cyanide+Hg	62	140	390	4.0	70	120	2.0
210	Acid, high SO_4	51	100	320	2.5	60	120	1.0
217	Acid, dextrin	54	110	390	3.0	70	120	2.0
	Average	53	120	360	3.6	65	120	1.5
	0.001 INCH							
206	Standard cyanide	82	220	720	5.0	110	170	4.5
209	Cyanide+Hg	91	160	720+	4.5	110	190	4.5
215	Acid, high SO_4	87	340	720	5.0	120	250	4.0
218	Acid, dextrin	88	270	720	5.0	110	250	4.5
	Average	87	250	720	4.9	110	220	4.5
219	Hot dip	81	80	360	3.5	90	250	4.0
	B. CADMIUM—0.0002 INCH							
304	Standard cyanide	17	720	720+	5	530	690+	2.5
307	Cyanide+gulac	17	340	560	5	680+	720+	4.5
310	Cyanide+gulac+Ni	16	720	720+	5	300	590	0
	Average	17	590	670+	5	500+	670+	2.3
	0.0005 INCH							
301	Standard cyanide	35	720+	720+	5	530+	720+	4.5
302	Cyanide, cath. pickle	34	720+	720+	5	600+	720+	4.5
303	Cyanide, anode pickle	33	720+	720+	5	660+	720+	4.5
308	Cyanide+gulac	32	720+	720+	5	600+	720+	4.5
311	Cyanide+gulac+Ni	31	720+	720+	5	520+	720+	3.0
	Average	33	720+	720+	5	580+	720+	4.2
	0.001 INCH							
305	Standard cyanide	63	720+	720+	5	540	720+	4.5
309	Cyanide+gulac	59	720+	720+	5	620+	720+	4.5
312	Cyanide+gulac+Ni	63	720+	720+	5	530	720+	4.0
	Average	62	720+	720+	5	560+	720+	4.3
	C. ZINC-CADMIUM ALLOY—0.0002 INCH							
402	10% of Cd	27	50	150	3	30	70	0

TABLE 12.—*Accelerated tests on zinc and cadmium coatings*—Continued

C. Zinc-Cadmium Alloy—0.0005 INCH

Set	Coating: Description	Atmospheric average score NY+P	Salt spray: Initial rust: To R=4	Salt spray: Initial rust: To R=0	Salt spray: Rating 100 hours R	Intermittent immersion: Initial rust: To R=4	Intermittent immersion: Initial rust: To R=0	Intermittent immersion: Rating 100 hours R
		Percent	hr	hr		hr	hr	
401	10% of Cd	64	200	600	5	90	160	1.5
404	8% of Cd	61	200	650	5	90	130	2.0
405	14% of Cd	59	150	460	5	90	120	1.5
	Average	61	180	570	5	90	140	1.7
	0.001 INCH							
403	10% of Cd	96	270	720+	5	100	110	3

2. RESULTS

Each result in table 12 represents the average of four similar specimens tested at different times. In general, the reproducibility in these tests was somewhat better than with nickel and chromium finishes, though there were appreciable variations in the periods required for initial rust to appear. The periods required for complete

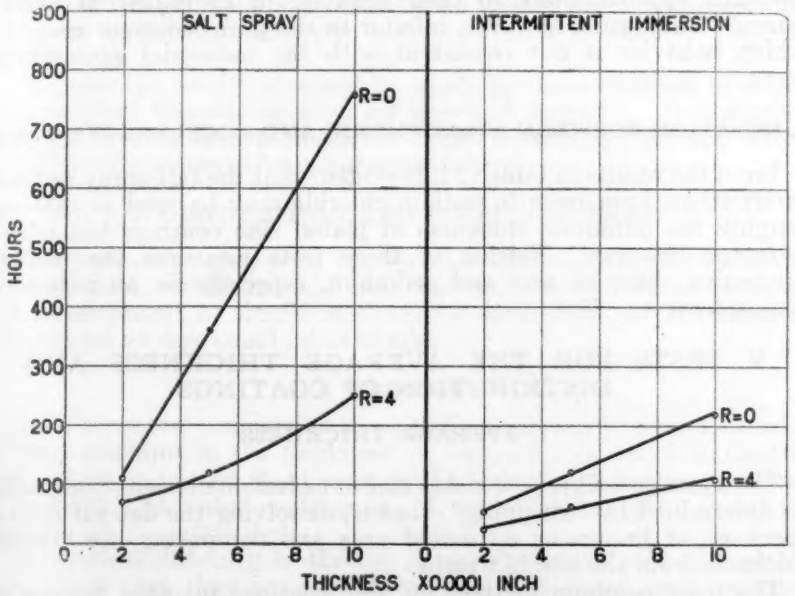

FIGURE 7.—*Rate of failure of zinc plated steel in accelerated tests, to* R=*4 (1 to 5 percent rust) and to* R=*0 (over 50 percent of rust).*

failure (that is, to a rating of 0, representing 50 percent or more of rust) were generally more consistent.

The results for zinc coatings, shown in table 12 and in figure 7, indicate that in both salt spray and intermittent immersion the time

of failure is a rough measure of the thickness. As the latter can be more conveniently measured by the dropping test [3], to be described, there is no advantage in using these accelerated tests, especially on thick coatings, for which long periods are required. In general, the tests were run continuously for one month (720 hours). Absence of rust at the end of that time is indicated in table 12 by "720+." Values such as 690+, which may represent an average of 660, and 720+ indicate that only part of the specimens of that set withstood the test for over 720 hours. In a few cases the test was continued for as much as 1,440 hours (2 months), but the results were no more conclusive. Changes in the method of plating produced no consistent differences in the results.

With intermittent immersion, electroplated zinc coatings failed in about half the time that was required in the salt spray. On the other hand, the hot-dipped coatings (set 219) failed in about the same time in both the spray and the immersion tests. Groesbeck and Tucker [13, p. 273] reported that electroplated zinc coatings failed more rapidly in a salt spray than in continuous immersion.

The results in table 12 fully confirm the well known high resistance of cadmium coatings to sodium chloride solutions in both the spray and immersion tests. Neither test is a reliable measure of the thickness of cadmium, as the 0.001-in. coatings showed initial failure in about the same time as did the 0.0005- or 0.0002-in. coatings.

In both of the accelerated tests, the zinc-cadmium alloys showed somewhat greater resistance than pure zinc coatings, which corresponds approximately to their behavior in an industrial atmosphere. They were, however, inferior to the pure cadmium coatings, which behavior is not consistent with the industrial atmospheric tests.

3. RELATION BETWEEN ATMOSPHERIC AND ACCELERATED TESTS

From the results in table 12 it is evident that the salt-spray test and intermittent immersion in sodium chloride may be used to measure roughly the minimum thickness of plated zinc coatings but not of cadmium coatings. Neither of these tests measures the relative protective value of zinc and cadmium, especially in an industrial atmosphere.

V. TESTS FOR THE AVERAGE THICKNESS AND DISTRIBUTION OF COATINGS

1. AVERAGE THICKNESS

The average thickness of either zinc or cadmium deposits can readily be determined by "stripping", that is, dissolving the deposit from a specimen of known or estimated area and computing the average thickness from the loss in weight.

The most common method for zinc coatings involves the use of hydrochloric acid containing antimony chloride. The same method and conditions are applicable to cadmium coatings. The solutions specified by the ASTM have the following composition [14]:

Solution a.—Antimony Chloride. Dissolve 20 g of antimony trioxide ((Sb_2O_3) or 32 g of antimony trichloride ($SbCl_3$) in 1,000 ml of chemically pure concentrated hydrochloric acid (sp gr 1.19).[4]

Solution b.—Hydrochloric Acid (HCl). Chemically pure concentrated hydrochloric acid (sp gr 1.19).[5]

Solution c.—Test Solution. This consists of 5 ml of solution a and 100 ml of solution b.

The specimen with a measured area is cleaned with an organic solvent, followed if necessary by light rubbing with magnesium oxide paste and thorough rinsing. It is dried and weighed, and then immersed in a suitable volume of the test solution until evolution of hydrogen practically ceases (usually in 15 to 30 seconds). The temperature of the solution should not exceed 38° C (100° F) during the test. The specimen is then rinsed and scrubbed under running water, rinsed with alcohol, wiped dry, dried at 100° C (212° F), and cooled. It is reweighed and the loss in weight is taken as the weight of zinc or cadmium on the specimen. The average thickness may be computed from the area stripped and the specific gravity of zinc (7.1), or of cadmium (8.6).

For stripping cadmium coatings a solution containing 120 g/liter of ammonium nitrate is sometimes used at a temperature slightly above room temperature, for example, 40° C (104° F). About 10 minutes is required to dissolve 0.001 in. of cadmium.

Another stripping solution for cadmium deposits contains 50 g/liter of ammonium persulphate and 100 ml/liter of concentrated ammonium hydroxide (sp gr 0.90), which should be freshly prepared before use. At room temperature about an hour is required to dissolve 0.001 in. of cadmium.

The average results obtained by applying these methods to duplicate weighed deposits on steel are shown in table 13. It is evident that the errors in these methods are almost never over 1 percent, which is sufficiently accurate for commercial testing.

2. DISTRIBUTION AND LOCAL THICKNESS

The present tendency to specify the minimum rather than the average thickness of zinc and cadmium coatings on steel necessitates the development of simple methods for measuring the thickness of the deposit on any small selected area.

(a) PREECE TEST

The Preece test (immersion in neutral copper sulphate) is a measure of the variations in the thickness of zinc coatings, which is used in spite of its admitted shortcomings [15]. Many of these objections do not apply to plated coatings, which are practically pure zinc, with no layer of zinc-iron alloy.

A practical difficulty in the use of the Preece test for zinc-plated coatings is that they are usually thinner than hot-dipped coatings. If, then, for example, only two 60-second dips are required, the precision of the method is only about 50 percent. This difficulty can be

[4] Chemically pure concentrated hydrochloric acid usually has a specific gravity of approximately 1.18, which is satisfactory for this test.
[5] See footnote 4.

TABLE 13.—*Accuracy of methods for stripping zinc and cadmium*

A. ZINC

Set	Description	Average thickness [1]	Average error (%)		
			$SbCl_3$	NH_4NO_3	$(NH_4)_2S_2O_8$
		Inch			
205	Standard cyanide	0.0002	−0.9		
202	do	.0005	+0.5		
208	Cyanide+Hg	.0005	−0.2		
210	Acid, high SO_4	.0005	+0.4		
217	Acid, dextrin	.0005	+1.2		
206	Standard cyanide	.001	+0.1		
	Average		+0.2		
	B. CADMIUM				
304	Standard	0.0002	+0.7	+0.1	+0.8
302	do	.0005	+0.1	+0.5	+0.9
308	Gulac	.0005	+1.2	+1.9	+0.9
311	Ni+gulac	.0005	+0.1	+0.3	+0.3
305	Standard	.001	+0.1	+0.2	+0.2
	Average		+0.4	+0.6	+0.6
	C. ZINC-CADMIUM ALLOY				
402	10% of Cd	0.0002	+2.6		
401	10% of Cd	.0005	+0.3		
404	8% of Cd	.0005	+0.8		
405	14% of Cd	.0005	+1.0		
403	10% of Cd	.001	+0.4		
	Average		+1.0		

[1] Based on the actual weights of metal deposited.

partly overcome by using shorter immersion periods, such as 15 seconds. Under these conditions the results are more reproducible, but are not directly comparable with those obtained in 1-minute dips; as four 15-second dips are not exactly equivalent to one 1-minute dip.

A more serious objection to the use of the Preece test for relatively thin electrodeposits is that if the coating on a given article is nearly uniform in thickness, an endpoint of adherent copper is not always obtained, even when the entire surface of the steel is exposed. This behavior results from the fact that the adherent copper is ordinarily deposited because the adjacent residual zinc acts as an anode with respect to the bare steel, which serves as the cathode. If, however, a thin uniform coating is removed in one immersion, no zinc is left to serve as the anode. This difficulty can be overcome by attaching to the test specimen a piece of zinc gauze or thin strips of zinc, whose presence will then cause deposition of adherent copper on exposed steel. This modification makes the method cumbersome. Therefore the Preece test is not recommended for testing plated zinc coatings having a minimum thickness of less than 0.0005 in.

It was found that it requires approximately four 1-minute dips for 0.001 in., two 1-minute dips for 0.0005 in., and three 15-second dips for 0.0002 in. As the individual values were not very concordant, no high accuracy should be attached to these values. They show that the time is approximately proportional to the thickness.

(b) DROPPING TESTS

Recent experience has shown that the rate of solution of a zinc or cadmium coating is more constant if the reagent is applied to the surface in successive drops than if the specimen is immersed in the solution. S. G. Clark [16] described such a method, in which an aqueous solution containing 100 g/liter of iodine and 200 g/liter of potassium iodide was allowed to fall at the rate of one drop per second upon the surface to be tested, until the steel was exposed. Under these conditions, 18 drops were required for 0.0001 in. of cadmium. This rate for cadmium was confirmed at this Bureau, and it was also found that with this solution 22 drops were required for 0.0001 in. of zinc.

This method was modified by Hull and Strausser [3], who substituted acidified ammonium nitrate solutions for the iodine. They found that with more rapid dropping (90 to 110 drops per minute), the rate of solution was practically independent of the rate of dropping. They therefore expressed their results in terms of the time required to dissolve the coatings. To simplify the calculations, they adjusted the composition of the various reagents so that a specified coating was dissolved at the rate of 0.000 01 in. per second. The tests were made at room temperature (20 to 30° C or 70 to 90° F). Temperature changes within this range had a neglible effect on the rate of solution. Simple apparatus for this test is shown in figure 8 (facing p. 193). Experiments made here subsequent to those reported by Hull and Strausser have shown that hot-dipped zinc coatings can be similarly tested with an appropriate reagent. On weighed specimens the following solutions yielded results that were accurate to ± 15 percent, which is a higher precision than is usual with the Preece test.

For zinc—

(1) Plated coatings (including those that contain small amounts of mercury):

Ammonium nitrate	100 g/liter.
Nitric acid (sp gr 1.42)	55 ml/liter.

(2) Hot-dipped coatings:

Ammonium nitrate	100 g/liter.
Hydrochloric acid (sp gr 1.180)	75 ml/liter.

For cadmium—

Ammonium nitrate	110 g/liter.
Hydrochloric acid (sp gr 1.180)	10 ml/liter.

The specimen to be tested is cleaned so that it is free from "water-break", and is then supported under the outlet tip so that the solution hits the spot to be tested and runs off quickly. The time required to expose the steel is measured with a stop-watch. In applying this and other tests to determine the minimum thickness, consideration should be given to those portions where the minimum thickness is most likely to occur.

(c) MICROSCOPIC MEASUREMENTS

For relatively hard metals such as copper and nickel, the measurement of metallographic cross sections at selected points is a very satisfactory method for determining the distribution and local thickness.

With soft metals like zinc and cadmium it is very difficult to avoid flow of the coating during the polishing of a cross section, even when a harder metal is deposited upon or clamped against the deposit to be examined. Results of numerous tests on coatings of known average thickness, whose distribution had been checked by dropping methods, were erratic. Considerable skill is required to obtain reliable microscopic measurements of either zinc or cadmium coatings.

(d) CHORD METHOD

F. C. Mesle [17] recently described a method for testing the thickness of plated coatings, which depends upon just cutting through the coating on a curved surface with a flat file, or on a plane surface with a precision grinding wheel of known radius. In either case the thickness of the coating, T, may be computed from the width of the chord, C (measured with a lens and scale) and the radius R of the object or grinding wheel, in accordance with the equation

$$T=\frac{C^2}{8R}$$

In effect, the method results in a mechanical instead of an optical magnification of the cross section of the deposits.

A detailed study of this method [18] was recently made at the National Bureau of Standards. It showed that under favorable conditions the accuracy of the method for various coatings, including zinc and cadmium on steel, is about 10 percent, which is at least equal to that obtained for zinc and cadmium by other methods. This method is not satisfactory for coatings less than 0.0002 in. thick.

VI. CONCLUSIONS

1. Thin coatings of either zinc or cadmium furnish better protection against corrosion of steel in most normal climates than do equally thin coatings of nickel or chromium [1].

2. In uncontaminated marine or rural atmospheres either zinc or cadmium coatings with a minimum thickness of 0.0005 in. furnish protection against corrosion for at least a few years.

3. In industrial locations both zinc and cadmium coatings fail in a comparatively short time. (Most of the following conclusions regarding atmospheric exposure are based on industrial exposure.)

4. In an industrial atmosphere cadmium coatings fail in from 65 to 75 percent of the time that is required for failure of zinc coatings of the same thickness.

5. In an industrial atmosphere alloy deposits that contain about 10 percent of cadmium and 90 percent of zinc have a slightly longer life than zinc and considerably longer than cadmium deposits.

6. In industrial locations the protective value of either zinc or cadmium coatings is practically proportional to their thickness.

7. Neither the methods used for preparing the steel employed in this investigation nor the variations made in the composition of the zinc-or cadmium-plating solutions had any effect on the protective value of the coating that was comparable with the effect of thickness.

8. Plated zinc coatings furnish about the same protection as hot-dipped zinc coatings *of the same thickness.*

9. In the salt-spray and intermittent-immersion tests, the time required for failure of zinc coatings is approximately proportional to the thickness.

10. Plated zinc coatings fail more rapidly in the intermittent immersion than in the salt spray test.

11. Neither the salt spray nor intermittent immersion furnishes a reliable criterion of thickness of cadmium coatings or of their protective value relative to that of zinc in an industrial atmosphere.

12. The average thickness of either zinc or cadmium coatings can be determined reliably from the loss in weight in the antimony chloride-hydrochloric acid stripping test; and of cadmium coatings by stripping in ammonium nitrate or ammonium persulphate.

13. The Preece test is a fairly reliable measure of the distribution (but not of the actual thickness) of plated zinc coatings over 0.0005 in. thick. It is not satisfactory for thinner coatings.

14. The dropping methods with an iodine solution or an ammonium-nitrate solution measure the local thickness and distribution of zinc and cadmium coatings with an accuracy of about 15 percent.

15. The "chord" method may be used to measure the local thickness of zinc and cadmium coatings with an accuracy of about 10 percent.

VII. REFERENCES

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